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Citation: *The Journal of Chemical Physics* **119**, 10814 (2003); doi: 10.1063/1.1621382

View online: <http://dx.doi.org/10.1063/1.1621382>

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Infrared spectra of *trans*-HOCO, HCOOH⁺, and HCO₂⁻ trapped in solid neon

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(Received 31 January 2003; accepted 2 September 2003)

When a Ne:HCOOH sample is codeposited at *ca.* 5 K with neon atoms that have been passed through a microwave discharge, new absorptions appear in the infrared spectrum of the resulting solid that can be assigned to *trans*-HOCO, *trans*-HCOOH⁺, and HCO₂⁻. The absorptions of *trans*-HOCO are readily identified by a comparison with those previously reported for that molecule trapped in solid argon. Preliminary assignments of infrared absorptions of HOCO⁺, confirmed in studies using another experimental system, are also suggested. The identifications of *trans*-HCOOH⁺ and of HCO₂⁻ are aided by study of the photodestruction characteristics of these products when the deposit is exposed to various wavelengths of visible and ultraviolet radiation, by an analysis of the spectra obtained from isotopically substituted samples, and by a comparison with the results of *ab initio* and density functional calculations. Three previously unidentified vibrational fundamentals of *trans*-HCOOH⁺ have been assigned, as have been four vibrational fundamentals of HCO₂⁻, in the inert, nonionic environment of solid neon. The CH-stretching fundamental of HCO₂⁻ appears at an exceptionally low frequency. The results of density functional calculations of the structures and vibrational fundamentals of *trans*-HCOOH⁺, HCO₂⁻, the W(C_{2v}) structure of C(OH)₂⁺, and *cis*- and *trans*-HCOOH⁻ are given. [DOI: 10.1063/1.1621382]

I. INTRODUCTION

The ions derived from formic acid—the simplest organic acid—are of interest in a variety of systems. Hayhurst and Kittelson¹ reported the presence of HOCO⁺, H₂CO₂⁻, and HCO₂⁻ in atmospheric pressure oxy-acetylene flames, in which HCO₂⁻ was a dominant anion species. The role of ions in the decomposition of formic acid adsorbed on surfaces has received considerable study. Moreover, uncharged HCOOH and products of the fragmentation of its cation, including HCO⁺ and HOCO⁺, have been found in interstellar matter.

Despite the importance of these ionic species, little is known about their vibrational energy levels. The first photoelectron band of HCOOH, initially studied by Brundle and co-workers,² has a structure with a spacing of approximately 1500 cm⁻¹, attributed to a CO-stretching vibration.^{3,4} Recent higher resolution studies of the photoelectron spectrum of HCOOH-*d_n* by Schwell, Leach, and co-workers^{5,6} permitted an assignment of several vibrational fundamentals of both the ground-state and excited-state species. The detection⁷ of an electron spin resonance signal of HCOOH⁻ requires that species to have at least a shallow potential minimum, but no other spectroscopic data are available for it. Over a wide energy range, the electron bombardment of gaseous formic acid leads to HCO₂⁻ as the predominant anion product.^{8,9} Early *ab initio* calculations by Chandrasekhar and co-workers¹⁰ established that HCO₂⁻, rather than HOCO⁻, is the lowest-energy structure. The most sophisticated calcu-

lations were those by Botschwina,¹¹ who included the study of anharmonic contributions to the vibrational fundamentals of HCO₂⁻ and DCO₂⁻. Detailed studies of the infrared and Raman spectra of polycrystalline HCOONa and DCOONa were reported by Kidd and Mantsch.¹² The photoelectron spectrum of HCO₂⁻, obtained by Kim and co-workers,¹³ included a hot band with a spacing of approximately 730 cm⁻¹, attributed to the ν_3 fundamental of the gas-phase anion.

An ongoing series of experiments in this laboratory has yielded infrared spectra for a number of molecular cations and anions stabilized in solid neon. For these studies, a suitable precursor molecule, contained in a several hundred-fold excess of neon, is codeposited at *ca.* 5 K with a beam of neon atoms that has been excited in a microwave discharge. The results of these experiments have recently been surveyed.¹⁴ All of the observations indicate that, because very few molecules enter the discharge region, atomization, extensive fragmentation, and isomerization of the parent molecule are minimal. The effective maximum excitation energy available for the photodissociation or photoionization corresponds to the energy of the highest member of the first group of excited energy levels of the neon atom, 16.85 eV. Electrons produced by photoionization are captured by atoms and molecules in the deposit, yielding detectable concentrations of anions.

II. EXPERIMENTAL DETAILS (REF. 15)

The formic acid samples used for these studies were the same as had been used for an earlier series of experiments.¹⁶

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The neon matrix gas (Spectra Gases, Research Grade, 99.999%) was used without further purification. Except that neon was substituted for argon, the sample preparation procedures were similar to those used in the earlier study. Most experiments were conducted using Ne:HCOOH mixtures of mole ratio 800, but one Ne:HCOOH=400 and one Ne:HCOOH=3200 experiment were also conducted. In order to obtain some oxygen-18 enrichment of the DCOOD, experiments were conducted on a Ne:DCOOD:D₂¹⁸O = 800:1:2 sample. As in an earlier study by Redington,¹⁷ the DCOOD and D₂¹⁸O were cocondensed in a volume that was sufficiently small that a liquid phase was present. This mixture was allowed to stand overnight before it was expanded into the sample bulb and neon was added.

The sample mixtures were codeposited at approximately 5 K with a similar amount of pure neon that had been excited by a microwave discharge before streaming from the pinhole in the end of a quartz discharge tube. Details of this deposition procedure and of the discharge configuration have been described previously.^{18,19}

The absorption spectra of the sample deposits were obtained using a Bomem DA3.002 Fourier transform interferometer with transfer optics that have been described previously.²⁰ Observations were conducted with a resolution of 0.2 cm⁻¹ between 400 and 5000 cm⁻¹ using a globar source, a KBr beamsplitter, and a wide-band HgCdTe detector cooled to 77 K. Data were accumulated for each spectrum over a period of at least 15 min. The resulting spectrum was ratioed against a similar one taken without a deposit on the cryogenic mirror. Under these conditions, the positions of the prominent, nonblended atmospheric water vapor lines between 1385 and 1900 cm⁻¹ and between 3620 and 3900 cm⁻¹, observed in a calibration scan, agreed to within 0.01 cm⁻¹ with the high-resolution values reported by Toth.²¹ Based on previous investigations, with this experimental configuration the standard uncertainty (type B) in the determination of the positions of absorption maxima for molecules trapped in solid neon is ±0.1 cm⁻¹ (coverage factor, $k=1$, i.e., 1σ).

Information on photoinduced changes in the matrix sample was obtained by exposing the deposit to various wavelength ranges of visible and ultraviolet radiation. In one study of a Ne:DCOOD sample, a tungsten background source and a 630 nm short-wavelength cutoff filter (Corning glass type 2403) were used. In all of the other studies, a medium-pressure mercury arc was used with a filter of Corning glass type 3389 or 7740 or without a filter to provide a short-wavelength cutoff of approximately 420, 280, or 250 nm, respectively.

III. RESULTS AND DISCUSSION

A. General survey

The infrared spectrum of a Ne:HCOOH sample codeposited with undischarged neon agreed well with that previously reported by Redington,¹⁷ with little evidence for an appreciable concentration of the dimer. Several infrared absorptions grew in intensity on unfiltered mercury-arc irradiation of the deposit. The most prominent of these were at 1599.5

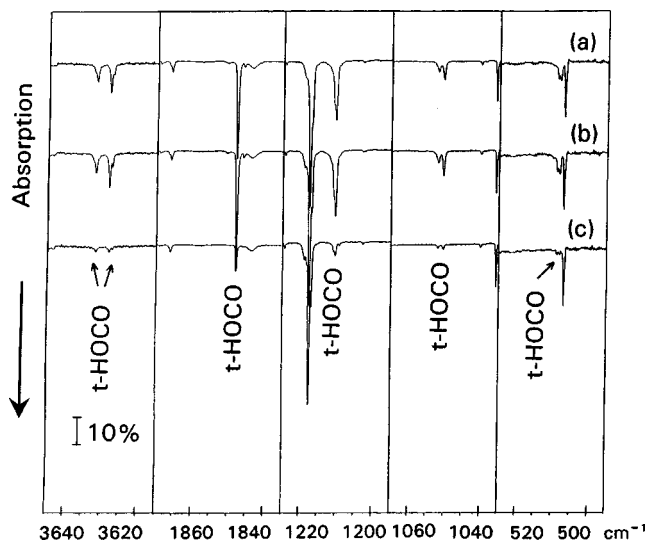


FIG. 1. Absorptions contributed by *trans*-HOCO to the infrared spectrum of the products of codeposition at ca. 5 K of 10.70 mmol Ne:HCOOH=3200 over a period of 280 min with 11.48 mmol of neon that had been passed through a microwave discharge. (a) Initial deposit. (b) 15 min mercury-arc irradiation, $\lambda > 420$ nm. (c) 15 min mercury-arc irradiation, $\lambda > 280$ nm.

and 2150.7 cm⁻¹, readily assigned to vibrations of the H₂O··CO complex,²² which is the predominant product of the 193 nm photodecomposition of HCOOH trapped in rare-gas matrices.²³

Another possible product is *cis*-HCOOH, which, unlike the more stable *trans*-isomer, has both H atoms on the same side of the central C–O bond. The strongest absorption of *cis*-HCOOH appears at 1244 cm⁻¹.²⁴ Moreover, the absorptions of that species disappeared with a half-life of only a few minutes. Such absorptions were not detected in the present experiments.

As in the similar argon-matrix experiments,¹⁶ a substantial yield of *trans*-HOCO was stabilized. The absorptions of this product observed in the initial deposit of the experiment for which Ne:HCOOH=3200 are shown in Fig. 1. As is also shown in that figure, the absorptions of *trans*-HOCO grew in intensity on irradiation of the deposit through the 420 nm cutoff filter and were destroyed when the sample was subsequently exposed to the mercury-arc radiation passed by the 280 nm cutoff filter.

Figure 2 shows other relatively prominent product absorptions that appeared below 2000 cm⁻¹ in the same experiment. The structured absorption between 1650 and 1670 cm⁻¹, contributed by isolated and complexed CO₂⁻,¹⁸ was readily destroyed by 420 nm cutoff radiation. Absorptions at 1497.7 and 679.3 cm⁻¹ diminished less readily on irradiation through the 420 nm cutoff filter. A prominent, rather broad absorption at 1630.6 cm⁻¹ grew in intensity as the deposit was exposed to radiation of an increasingly higher energy. This absorption is assigned to the *R*(0) band of ν_2 of H₂O,²⁵ which desorbs from the walls of the deposition system during the several-hour deposition period typical of these experiments. Prominent absorptions at 1626.4 and 1628.9 cm⁻¹ grew on irradiation through the 420 and 280 nm cutoff filters but were destroyed by unfiltered mercury-arc radiation. Less intense absorptions at 1325.8, 1323.0, and 744.1 cm⁻¹ be-

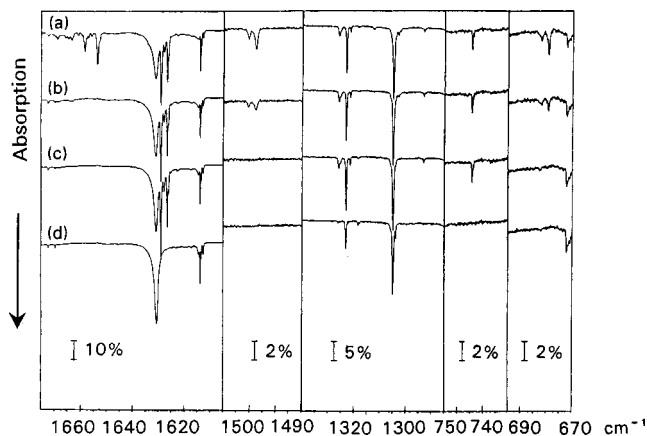


FIG. 2. Selected product absorptions below 1700 cm^{-1} in the infrared spectrum of the products of codeposition at *ca.* 5 K of $10.70\text{ mmol Ne:HCOOH}=3200$ over a period of 280 min with 11.48 mmol of neon that had been passed through a microwave discharge. (a) Initial deposit. (b) 15 min mercury-arc irradiation, $\lambda > 420\text{ nm}$. (c) 15 min mercury-arc irradiation, $\lambda > 280\text{ nm}$. (d) 19 min unfiltered mercury-arc irradiation.

haved similarly. (The sharp, relatively prominent peak at 1323.0 cm^{-1} that was approximately halved in intensity on unfiltered irradiation was contributed in part by HCOOH. Although HCOOH itself experienced slow photodestruction, the relative invariance of the somewhat more prominent HCOOH peak at 1304 cm^{-1} indicates that a product absorption must also contribute to the peak at 1323.0 cm^{-1} .)

Other product absorptions that appeared in the same experiment between 2000 and 3500 cm^{-1} are shown in Fig. 3. A peak at 3412.1 cm^{-1} decreased in intensity on 420 nm cutoff irradiation. A more prominent absorption at 2455.7 cm^{-1} grew on 420 and 280 nm cutoff irradiation, but was destroyed by unfiltered mercury-arc irradiation. A relatively sharp peak at 2063.6 cm^{-1} diminished in intensity on 420

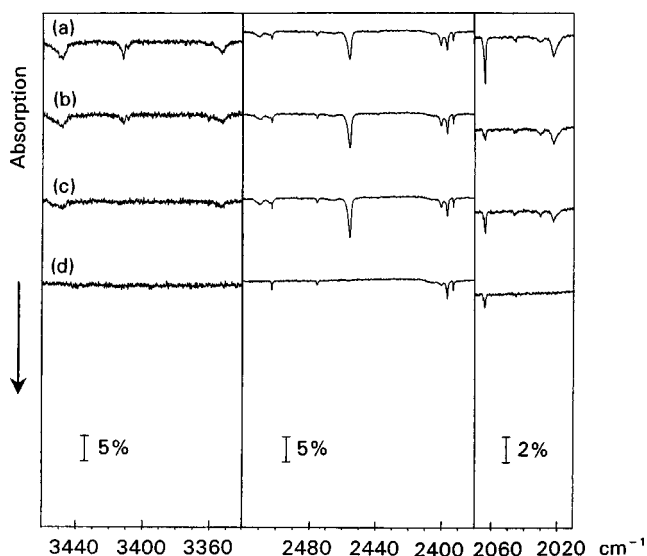


FIG. 3. Selected product absorptions between 2000 and 3500 cm^{-1} in the infrared spectrum of the products of codeposition at *ca.* 5 K of $10.70\text{ mmol Ne:HCOOH}=3200$ over a period of 280 min with 11.48 mmol of neon that had been passed through a microwave discharge. (a) Initial deposit. (b) 15 min mercury-arc irradiation, $\lambda > 420\text{ nm}$. (c) 15 min mercury-arc irradiation, $\lambda > 280\text{ nm}$. (d) 19 min unfiltered mercury-arc irradiation.

nm cutoff irradiation, grew again on 280 nm cutoff irradiation, and once more decreased on unfiltered irradiation. This photolytic behavior was unique. Beyond the range of Fig. 3 is a weak to moderately intense absorption at 4078.2 cm^{-1} , which was destroyed by the radiation of wavelength longer than 420 nm .

The positions and approximate relative intensities of the new absorptions that are characteristic of the codeposition of a $\text{Ne:HCOOH}=800$ sample with discharged neon are summarized in the first column of Table E-1, a part of the EPAPS files that are supplementary to this paper.²⁶ Peaks that grew on unfiltered mercury-arc irradiation of a Ne:HCOOH sample codeposited with undischarged neon were omitted from that table.

B. Isotopic substitution

Positive spectroscopic identifications in matrix isolation experiments are greatly facilitated by isotopic substitution studies. Although heavily oxygen-18 enriched formic acid was not readily accessible, studies on other isotopomers of HCOOH provide sufficient information for several product identifications.

The new absorptions that appeared in an experiment in which a $\text{Ne:H}^{13}\text{COOH}=800$ sample was codeposited with discharged neon are summarized in the second column of Table E-1 of Ref. 26. The absorption that appeared at 1497.7 cm^{-1} in the unsubstituted system, shown in Fig. 4(a), experiences a relatively large carbon-13 isotopic shift, to 1459.2 cm^{-1} [Fig. 4(b)]. Similarly, there is a large carbon-isotopic shift in the sharp absorptions near 1625 cm^{-1} [Fig. 5(a)], which move to 1582.6 and 1585.0 cm^{-1} [Fig. 5(b)]. The anticipated absorption of $^{13}\text{CO}_2^-$ at 1614.1 cm^{-1} [Fig. 5(b)] is overlapped by the sharp, relatively prominent absorption of NO_2 impurity, which in that experiment resulted from a small leak in the discharge tube. Spectral overlap near 1300 cm^{-1} no longer occurred; a product absorption at 1302.1 cm^{-1} had photodestruction behavior similar to that of the 1582.6 and 1585.0 cm^{-1} peaks.

The product absorptions observed in studies of Ne:DCOOH and Ne:DCOOD samples codeposited with discharged neon are summarized in columns 3 and 4 of Table E-1 of Ref. 26. Background spectra indicated that a significant amount of DCOOH was present in the DCOOD experiment, presumably because of ready isotopic exchange with H_2O adsorbed on the walls of the deposition system, and that there was also some DCOOD in the DCOOH sample. The spectra of both isotopomers corresponded well with those reported by Redington.¹⁷ Several product absorptions were readily assigned to *trans*-DOC₂O. As is shown in Fig. 6, these absorptions, like those of *trans*-HOCO, grew on 420 nm cutoff irradiation but were destroyed by 280 nm cutoff radiation.

Other product absorptions that appeared below 1700 cm^{-1} in the spectrum of a $\text{Ne:DCOOD}=800$ sample are shown in Fig. 7. A detail of the absorption pattern near 1500 cm^{-1} is also shown in Figs. 4(c) and 4(d). A pair of approximately equally intense, rather broad absorptions at 1486.7 and 1489.6 cm^{-1} was resolved. Since in the analogous ex-

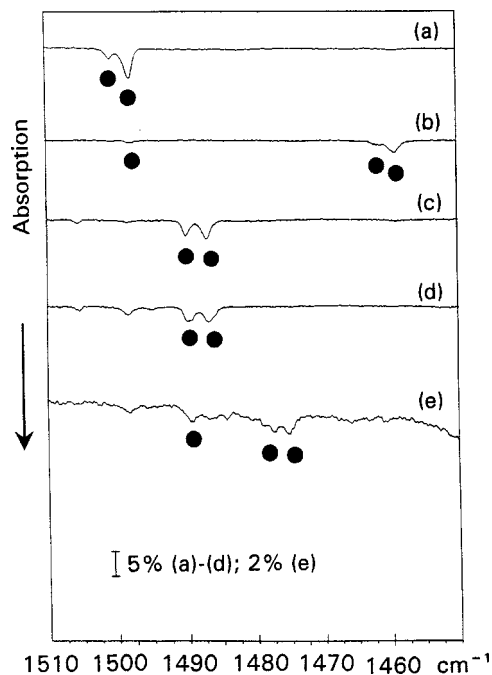


FIG. 4. Product absorptions between 1450 and 1510 cm^{-1} in the infrared spectra of various isotopically substituted Ne: formic acid samples codeposited at *ca.* 5 K with neon atoms that had been excited in a microwave discharge. ● diminishes on mercury-arc irradiation, $\lambda > 420$ nm. (a) 7.67 mmol Ne:HCOOH=800 codeposited over a period of 199 min with 8.27 mmol discharged neon. (b) 7.77 mmol Ne:H¹³COOH=800 codeposited over a period of 190 min with 7.89 mmol discharged neon. (c) 7.77 mmol Ne:DCOOH=800 codeposited over a period of 200 min with 8.18 mmol discharged neon. (d) 8.75 mmol Ne:DCOOD=800 codeposited over a period of 222 min with 9.05 mmol discharged neon. (e) 9.34 mmol Ne:DCOOD:D₂¹⁸O=800:1:2 codeposited over a period of 240 min with 10.28 mmol discharged neon.

periment on an unsubstituted sample the peak at 1497.7 cm^{-1} predominated, it is likely that this pair represents overlapping contributions of two different products. As is shown not only in Fig. 7 but also in Figs. 5(c) and 5(d), the peaks at 1626.4 and 1628.9 cm^{-1} characteristic of the unsubstituted product were replaced by a single pair of new absorptions, at 1622.5 and 1625.0 cm^{-1} . The 1628.9 cm^{-1} peak of the unsubstituted product persisted, but the 1626.4 cm^{-1} peak of the latter species would have been overlapped by the new 1625.0 cm^{-1} absorption. Such behavior suggests that only a single H (or D) atom contributes to the vibration that gives rise to this absorption. There is still interference from the absorption of formic acid near 1300 cm^{-1} for partially deuterium-substituted samples. However, as is shown in Fig. 7, a new absorption, destroyed by unfiltered mercury-arc radiation, appeared at 1309.1 cm^{-1} . A weak, photosensitive absorption appeared in the deuterium-substituted systems at 857.6 cm^{-1} , on the high-frequency side of a rather broad background absorption, and weak, photosensitive structured absorption appeared at 902.3 cm^{-1} . Also shown in Fig. 7 are a weak product absorption at 736.9 cm^{-1} that was destroyed by unfiltered mercury-arc radiation, a pair of absorptions at 676.0 and 678.9 cm^{-1} that diminished in intensity on 420 nm cutoff irradiation, and a new absorption at 530.9 cm^{-1} , with a less intense companion at 533.5 cm^{-1} , which diminished slightly on 420 nm cutoff irradiation.

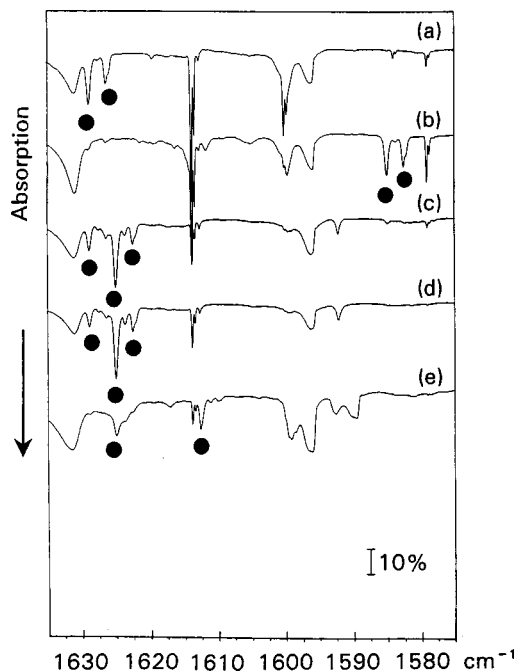


FIG. 5. Product absorptions between 1575 and 1635 cm^{-1} in the infrared spectra of various isotopically substituted Ne: formic acid samples codeposited at *ca.* 5 K with neon atoms that had been excited in a microwave discharge. ● diminishes on unfiltered mercury-arc irradiation. (a) 7.67 mmol Ne:HCOOH=800 codeposited over a period of 199 min with 8.27 mmol discharged neon. (b) 7.77 mmol Ne:H¹³COOH=800 codeposited over a period of 190 min with 7.89 mmol discharged neon. (c) 7.77 mmol Ne:DCOOH=800 codeposited over a period of 200 min with 8.18 mmol discharged neon. (d) 8.75 mmol Ne:DCOOD=800 codeposited over a period of 222 min with 9.05 mmol discharged neon. (e) 9.34 mmol Ne:DCOOD:D₂¹⁸O=800:1:2 codeposited over a period of 240 min with 10.28 mmol discharged neon.

Still other product absorptions that appeared above 1700 cm^{-1} in the Ne:DCOOD experiments are shown in Fig. 8. A sharp, relatively prominent peak at 2612.2 cm^{-1} was virtually unchanged on near-ultraviolet irradiation of the deposit, but was considerably diminished in intensity on unfiltered mercury-arc irradiation. Although, like the absorptions of

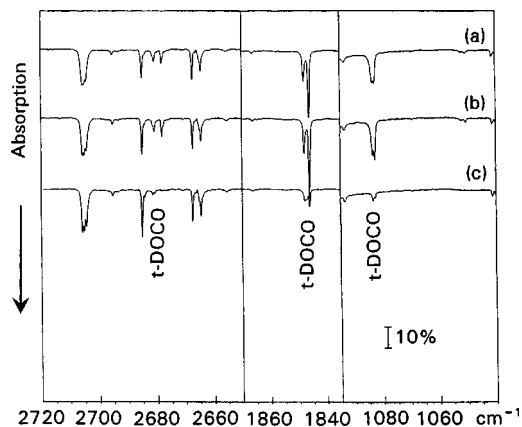


FIG. 6. Absorptions contributed by *trans*-DOCO to the infrared spectrum of the products of codeposition at *ca.* 5 K of 8.75 mmol Ne:DCOOD=800 over a period of 222 min with 9.05 mmol of neon that had been passed through a microwave discharge. (a) Initial deposit. (b) 15 min mercury-arc irradiation, $\lambda > 420$ nm. (c) 15 min mercury-arc irradiation, $\lambda > 280$ nm.

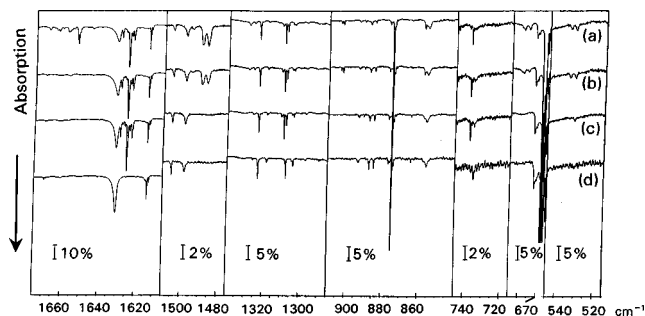


FIG. 7. Selected product absorptions below 1700 cm^{-1} in the infrared spectrum of the products of codeposition at *ca.* 5 K of 8.75 mmol Ne:DCOOD=800 over a period of 222 min with 9.05 mmol of neon that had been passed through a microwave discharge. (a) Initial deposit. (b) 15 min mercury-arc irradiation, $\lambda > 420\text{ nm}$. (c) 15 min mercury-arc irradiation, $\lambda > 280\text{ nm}$. (d) 18 min unfiltered mercury-arc irradiation.

trans-HOCO, some of the structure near 2530 and 2570 cm^{-1} grew on tungsten-lamp irradiation of the deposit through a 630 nm cutoff filter and decreased on subsequent mercury-arc irradiation through a 280 nm cutoff filter, consideration of the expected positions^{16,27} of all of the fundamentals of *trans*-DOCOC did not disclose any binary combination bands, which could account for either of these absorptions. In contrast, the weak to moderately intense peak at 2521.6 cm^{-1} , like the peaks at 1486.7 , 1489.6 , and 533.5 cm^{-1} , diminished in intensity on tungsten-lamp irradiation of the deposit through the 630 nm cutoff filter. The weak to moderately intense absorption at 2452.5 cm^{-1} decreased in intensity when the sample was exposed to 280 nm cutoff radiation, indicating that it cannot be correlated with the 2455.7 cm^{-1} product absorption characteristic of unsubstituted samples. Still another weak to moderately intense product absorption that diminished in intensity on irradiation of the deposit through the 280 nm cutoff filter appeared at 2023.2 cm^{-1} .

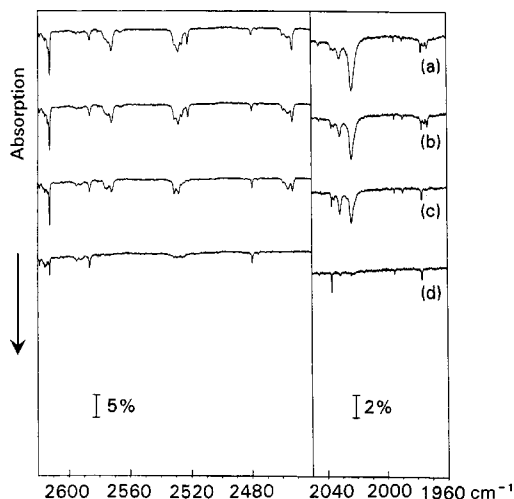


FIG. 8. Selected product absorptions between 1960 and 2620 cm^{-1} in the infrared spectrum of the products of codeposition at *ca.* 5 K of 8.75 mmol Ne:DCOOD=800 over a period of 222 min with 9.05 mmol of neon that had been passed through a microwave discharge. (a) Initial deposit. (b) 15 min mercury-arc irradiation, $\lambda > 420\text{ nm}$. (c) 15 min mercury-arc irradiation, $\lambda > 280\text{ nm}$. (d) 18 min unfiltered mercury-arc irradiation.

TABLE I. Absorptions (cm^{-1}) assigned to *t*-HOCO and *t*-DOCOC.

Species	Sym.	Vib.	<i>ab initio</i> ^a	Gas	Ne matrix ^b	Ar matrix ^c
<i>t</i> -HOCO	<i>a'</i>	1	3728	3635.70^d	3628.0	3602.9
		2	1903	1852.57^e	1848.0	1843.6
		3	1279		1210.4	1211.2
		4	1084		1050.4	1064.6
		5	605			
<i>t</i> -DOCOC	<i>a''</i>	6	538		508.1	515
		<i>a'</i>	1		2684.10^f	2678.1
		2		1851.65^e	1846.2	1841.7
		3			1082.6	1092.6

^aCCSD(T)/6-31G(d). Reference 29.

^bThis work. Based on previous investigations, the standard uncertainty (Type B) in the frequency measurement is $\pm 0.1\text{ cm}^{-1}$ (coverage factor, $k = 1$; i.e., 1σ).

^cReference 16.

^dReference 30.

^eReference 31.

^fReference 32.

As is illustrated by Fig. 4(e), significant oxygen-18 inclusion in the formic acid was achieved for a Ne:DCOOD: $D_2^{18}O$ sample. Although the signal-to-noise ratio was low, a pair of new absorptions appeared at 1475.2 and 1477.4 cm^{-1} . Figure 5(e) shows another new absorption, at 1612.6 cm^{-1} . Using a similar procedure, Redington¹⁷ found it possible to exchange both oxygen atoms of formic acid samples. Because the sampling conditions in the present experiments did not favor an extensive O-atom isotopic exchange, a single O-atom substitution is expected to predominate. The appearance of a single new absorption at 1612.6 cm^{-1} suggests that its carrier possesses either a single oxygen atom or two symmetrically equivalent oxygen atoms.

C. Infrared spectrum of *trans*-HOCO

The first identification of *trans*-HOCO, together with that of *cis*-HOCO, was that obtained by Milligan and Jacox²⁸ in studies of the vacuum ultraviolet photolysis of H_2O in a CO matrix. In a later argon-matrix study of the infrared spectrum of *trans*-HOCO,¹⁶ vibrations involving the OH bond were found to be significantly perturbed by the interaction with a CO matrix. Subsequent *ab initio* calculations^{27,29} of the fundamental vibration frequencies of *trans*-HOCO agree well with the argon-matrix values. The OH-stretching fundamental of gas-phase *trans*-HOCO has been observed by Petty and Moore³⁰ using a difference-frequency laser system, and the C=O stretching fundamental of the gas-phase molecule has been reported by Sears and co-workers,³¹ who used a diode laser. The corresponding gas-phase band centers of *trans*-DOCOC were also determined.^{31,32} The positions of the vibrational fundamentals of *trans*-HOCO and *trans*-DOCOC determined in the gas phase and in neon and argon matrices are summarized in Table I, together with the harmonic vibrational frequencies obtained by Francisco²⁹ in CCSD(T)/6-31G(d) calculations for *trans*-HOCO. The agreement is very good.

The failure to detect any candidate peaks in the 50 cm^{-1} region below the especially prominent 1848 cm^{-1} C=O

stretching fundamental of *trans*-HOCO suggests that little if any *cis*-HOCO is stabilized.

D. Infrared spectra of cations

Both photoionization and dissociative photoionization of formic acid can occur below the 16.85 eV effective energy limit of the present experiments. The first ionization energy of *trans*-HCOOH is well established to equal 11.329(2) eV,⁵³ and the onset of the production of HCOOH⁺ in its \tilde{A} state is at 12.38 eV.^{5,6} The appearance energy of CHO₂⁺ from HCOOH^{34,35} corresponds closely to the origin of the \tilde{A} state of HCOOH⁺. Mass analysis of the ion products from HCOOH has consistently demonstrated the predominance of CHO₂⁺ over a wide energy range. Although Warneck³⁵ found that the appearance energy of the HCO⁺ fragment ion from HCOOH lies at 12.79(3) eV, it is a minor product. Warneck also found the onset of OH⁺ production from HCOOH at 17.97(6) eV, above the effective energy of neon atoms in the discharge sampling configuration of these experiments. In light of these studies, the cations that are most likely to be stabilized in the present experiments are HCOOH⁺ and CHO₂⁺.

The growth in the intensities of the absorptions of rotating water as the deposit is exposed to visible and ultraviolet radiation of increasing photon energy, illustrated by the behavior of the 1630.6 cm⁻¹ absorption shown in Figs. 2 and 7, has been attributed³⁶ to a decrease in the magnitude of the ion field as photodetachment from anions and electron combination with cations proceeds.

The infrared absorption at 1497.7 cm⁻¹ corresponds closely with a structure having a spacing of approximately 1500 cm⁻¹ in the first photoelectron band of HCOOH.^{3,5,6} Vibrational fundamental absorptions near 1500 cm⁻¹ are comparatively rare. Thus, the product absorptions shown in Fig. 4 suggest the presence of HCOOH⁺.

The few available *ab initio* calculations of the fundamental vibrations of HCOOH⁺ have been at either the Hartree-Fock³⁷ or the MP2⁶ level. However, a recent study by Byrd and co-workers³⁸ indicates that, because of the importance of electron correlation, neither of these levels is adequate for determining the positions of ground-state vibrational fundamentals of free radicals. For such species, *ab initio* calculations at the CCSD or CCSD(T) level and density functional calculations using the B3LYP procedure are considerably more satisfactory. For this reason and because experiments on other systems have demonstrated the importance of considering not only the positions of the fundamentals of the unenriched molecule but also the patterns of both deuterium and heavy-atom isotopic shift in order to obtain positive identifications,^{39,40} we have conducted a series of calculations using the GAUSSIAN 98 program package.⁴¹ We report density functional calculations using the unrestricted B3LYP procedure,⁴² together with a 6-311+G(2*d*,*p*) basis set or with the correlation-consistent polarized valence double-zeta basis set (cc-pVDZ) developed by Dunning.⁴³ Like uncharged formic acid, the cation has *cis*- and *trans*-isomers, with the *trans*-isomer lower in energy than the *cis*-

The structures obtained in our calculations for the *trans*-

formic acid cation are compared with the experimental structure of uncharged *trans*-formic acid⁴⁴ and with the structure obtained from MP2 calculations by Leach and co-workers⁶ in Table E-2 of Ref. 26. The most significant difference from the neutral is the change in the two CO bond distances, which approach equality. The OH bond length of the cation is somewhat greater than that of the neutral.

The fundamental vibrational frequencies calculated for various isotopomers of *trans*-formic acid cation are summarized in Table E-3 of Ref. 26. This table also includes experimental values obtained in the gas-phase photoelectron spectroscopic study by Schwell, Leach, and co-workers,^{5,6} as well as neon-matrix identifications made in the following discussion and as a result of studies using Ne:H₂:CO₂ samples, reported in the accompanying paper.⁴⁵ Values obtained in this latter study are marked in Table E-3 by an asterisk. (In that table and the following discussion conventional spectroscopic notation, in which vibrations of a given molecule within each symmetry block are numbered sequentially, with the highest-frequency vibration having the lowest number, is adopted.) The ν_3 , ν_4 , ν_5 , and ν_6 fundamentals of HCOOH⁺ and its isotopomers are quite strongly mixed. The behavior of the frequencies and infrared intensities on isotopic substitution, summarized in Table E-3, gives information regarding the type of vibration associated with each of the infrared absorptions. The calculated frequencies given by Leach and co-workers⁶ are in reasonable agreement with the values obtained in the B3LYP calculations of the present study.

The most prominent absorption should be that of ν_1 , with a calculated intensity of approximately 300 km/mol. Other absorptions with calculated infrared intensities greater than 100 km/mol are those corresponding to ν_2 , ν_3 , ν_6 , and ν_9 .

The OCO antisymmetric stretching absorption, ν_3 , is calculated to lie at 1530 cm⁻¹ [6-311+G(2*d*,*p*)] or at 1557 cm⁻¹ (cc-pVDZ). Its calculated carbon-13 shift is 41.0 or 42.3 cm⁻¹, respectively, which compares well with the 38.5 cm⁻¹ shift observed for the 1497.7 cm⁻¹ infrared absorption. The calculated shift of ν_3 of DCOOD⁺ from the corresponding fundamental of HCOOH⁺ is 14.5 cm⁻¹ [6-311+G(2*d*,*p*)] or 11.3 cm⁻¹ (cc-pVDZ), compared to a measured shift of 11.7 cm⁻¹ (cf. Table E-3). Therefore, the isotopic shift pattern shown in Fig. 4 is appropriate for the OCO antisymmetric stretching fundamental of the *trans*-formic acid cation.

The absorption at 3412.0 cm⁻¹ behaves appropriately for assignment to ν_1 , the OH-stretching fundamental of *trans*-HCOOH⁺. The calculated position for the harmonic fundamental is 3594 cm⁻¹ [6-311+G(2*d*,*p*)] or 3558 cm⁻¹ (cc-pVDZ). Anharmonicity would lower the observed position by at least 100 cm⁻¹. If the absorption at 2521.6 cm⁻¹ in the DCOOD experiments is assigned as the OD-stretching fundamental of DCOOD⁺, the ratio (OD/OH) of the two stretching frequencies would equal 0.739. The corresponding harmonic ratio for either basis set equals 0.729, and the usual effect of anharmonicity is to increase the magnitude of that ratio somewhat.

Proton sharing with the neon matrix may decrease the

OH-stretching fundamental frequency of HCOOH^+ . A proton affinity of 623.4 kJ/mol has been reported⁴⁶ for HOCO . This value may be compared with the proton affinity of OH, 593.2 kJ/mol.⁴⁷ The neon-matrix shifts observed by Forney and co-workers⁴⁸ for the two OH-stretching fundamentals of H_2O^+ amount to 0.9% and 1.2%. If the proton affinity of the HCO_2 isomer is near 600 kJ/mol, the neon-matrix shift in the OH-stretching fundamental of HCOOH^+ should also be approximately 1%, or 35 cm^{-1} .

The ν_6 fundamental of HCOOH^+ is expected to contribute a relatively prominent infrared absorption near 1179 cm^{-1} [6-311+G(2d,p)] or 1166 cm^{-1} (cc-pVDZ). This fundamental should lie only between 25 and 50 cm^{-1} below ν_5 , with which it should be strongly mixed. Accordingly, the two isotopic substitution patterns summarized in Table E-3 of Ref. 11 differ considerably, and the intensities for the various isotopomers are irregular. The isotopic shift obtained for this fundamental of $\text{HC}^{18}\text{O}^{18}\text{OH}^+$ (for which the extent of mixing is greatest) in the UB3LYP/6-311+G(2d,p) calculation, 15.1 cm^{-1} , matches the observed shift of 14 cm^{-1} much better than does the 5.8 cm^{-1} shift predicted by the UB3LYP/cc-pVDZ calculation.

The absorption at 679.3 cm^{-1} may be contributed either by $(\text{CO}_2)_2^-$ or by the $\nu_9(a'')$ torsional vibration of HCOOH^+ , calculated to appear near 710 cm^{-1} . A weak absorption at 679.3 cm^{-1} and a very weak absorption at 674.0 cm^{-1} have been assigned⁴⁹ to $(\text{CO}_2)_2^-$. The carbon-13 substituted dimer anion had its absorption at 664.8 cm^{-1} . In the experiment on H^{13}COOH , the absorption shifted to 676.6 cm^{-1} , excluding the dimer anion as its carrier. In the DCOOH experiments the absorption shifted to 676.1 cm^{-1} , requiring that its carrier possess at least one H atom and suggesting its contribution by DCOOH^+ . In the DCOOD experiments, a weak absorption with photodestruction behavior similar to those of the peaks attributed to HCOOH^+ appeared at 530.9 cm^{-1} , with a satellite at 533.5 cm^{-1} . These absorptions correspond well with the expected position of the $\nu_9(a'')$ absorption of DCOOD^+ , calculated to lie near 550 cm^{-1} .

Although ν_2 , the CH-stretching fundamental of HCOOH^+ , is calculated to have a significant intensity, no suitable absorptions were detected in the region between 2900 and 3100 cm^{-1} .

The observed positions for the absorptions below 2500 cm^{-1} that have been attributed to isotopomers of HCOOH^+ are compared in Table E-3 of Ref. 26 with the positions obtained from the UB3LYP/cc-pVDZ calculations, scaled so that the values for the unenriched molecule match the observed frequencies. (The OH-stretching vibration of HCOOH^+ is relatively unmixed with the lower-frequency vibrations and, therefore, is insensitive to isotopic substitutions in other parts of the molecule.) Except for singly oxygen-18 enriched DCOOD^+ , the oxygen-18 shifts were obtained from experiments on isotopically enriched Ne:H_2 (or D_2): CO_2 samples.⁴⁵ In order to minimize relatively large deviations due to anharmonicity, the OD deformation and torsion fundamentals of heavy-atom substituted DCOOD^+ were scaled to the values for unenriched DCOOD^+ . Except for DCOOD^+ , all of the observed positions of the OCO

TABLE II. Positions (cm^{-1}) of vibrational fundamentals of $t\text{-HCOOH}^+$ and $t\text{-DCOOD}^+$.

Species	Sym.	Vib.	UB3LYP/			
			ROHF-MP2 ^a	cc-pVDZ	Gas phase ^a	Ne matrix ^b
$t\text{-HCOOH}^+$	a'	1	3658	3558.4		3412.0
		2	3133	2992.5	3026(20)	
		3	1640	1557.0	1495(20)	1497.7
		4	1414	1370.8		
		5	1223	1212.2	1196(20)	
		6	1190	1166.5		1143.7
		7	525	471.3	510(20)	
	a''	8	1046 ^c	995.6		
$t\text{-DCOOD}^+$	a'	9	721 ^c	717.7		679.3
		1	2666	2593.8		2521.6
		2	2314	2201.6	2304(20)	
		3	1625	1545.7	1472(20)	1486.7
		4	1291	1267.9	1250(20)	
		5	996	983.2	965(20)	
		6	890	858.0		855.3
		7	485	439.7	447(20)	
	a''	8	863 ^c	827.5		
	9	562 ^c	555.5		530.9	

^aReferences 5, 6.

^bThis work. Based on previous investigations, the standard uncertainty (Type B) in the frequency measurement is $\pm 0.1 \text{ cm}^{-1}$ (coverage factor, $k = 1$; i.e., 1σ).

^cUHF calculation.

antisymmetric stretching fundamental are somewhat higher than the calculated values. Nevertheless, the agreement is sufficiently close to support the assignment. The disparity for the OH-deformation fundamental of $\text{HC}^{18}\text{O}^{18}\text{OH}^-$ is attributed to vibrational mixing. For the other isotopomers, the agreement of the observed and scaled positions of the OH(D)-deformation fundamental is good. The isotopic shift pattern observed for the torsional fundamental also corresponds well with that calculated for HCOOH^+ .

In summary, a detailed consideration of the isotopic substitution pattern supports the assignments here proposed for several vibrational fundamentals of HCOOH^+ . These assignments are summarized in Table II for $trans\text{-HCOOH}^+$ and $trans\text{-DCOOD}^+$. The infrared assignments and those obtained by Schwell, Leach, and co-workers^{5,6} are, for the most part, complementary. The experimental values proposed by Schwell and Leach on the basis of combination band analysis for the CH- and CD-stretching fundamentals, which exceed the calculated (UB3LYP/cc-pVDZ) harmonic fundamental frequencies, are probably too high. The anharmonic correction for the CH-stretching fundamental is likely to lower the observed position of ν_2 by more than 100 cm^{-1} , widening the disparity. Alternatively, the 3026(20) cm^{-1} separation in the photoelectron spectrum of HCOOH^+ may correspond to $2\nu_3$, and the 2304(20) cm^{-1} separation in the photoelectron spectrum of DCOOD^+ may correspond to $\nu_3 + \nu_6$.

Candidate absorptions for assignment to HOCO^+ were observed in the present series of experiments. However, there are ambiguities in the identification of their carrier, and data did not suffice for correlations in the deuterium-substituted systems. Studies reported in the accompanying paper on the $\text{Ne:H}_2:\text{CO}_2$ system,⁴⁵ for which oxygen-18 iso-

topic substitution was readily accessible and a somewhat higher yield of HOCO⁺ was obtained, support the assignment of three fundamentals of HOCO⁺ which is included in Table E-1 of Ref. 26.

Other CH₂O₂⁺ isomers may also have contributed to the product spectrum. Uggerud and co-workers⁵⁰ explored portions of the CH₂O₂⁺ potential energy surface using UHF/4-31G geometry optimization followed by MP3/6-31G* energy calculations. They found five stable structures, all with a plane of symmetry. Of these, C(OH)₂⁺ was 9 kJ/mol more stable than HCOOH⁺. We attempted two different UB3LYP calculations of the structure and vibrational fundamentals of C(OH)₂⁺. The results are summarized in Tables E-4 and E-5 of Ref. 26. The present experiments provide no consistent evidence for either of these two isomers of C(OH)₂⁺.

E. Infrared spectra of anions

Evidence suggests that HCOOH⁻ has a stable potential minimum, but little is known about its properties. We conducted calculations at the UB3LYP level using the aug-cc-pVDZ basis set. Like the cation and the neutral, the anion was found to be planar, with *cis*- and *trans*-isomers that are very close in energy. The structures and vibrational frequencies obtained in these calculations for *cis*- and *trans*-HCOOH⁻ are summarized in Tables E-6 and E-7 of Ref. 26. Absorptions matching the calculated patterns were not identified in the present experiments.

The much more stable formate anion, HCO₂⁻, is energetically accessible in these experiments. Photoionization of HCOOH by 16.85 eV radiation can produce electrons with as much as 5.5 eV excess energy. Pelc⁹ observed the onset at 1.15(5) eV and a maximum at 1.25 eV in the formation of HCO₂⁻ from dissociative capture of monoenergetic electrons by HCOOH.

Photodetachment of HCO₂⁻ is likely to require exposure of the matrix-isolated anion to unfiltered mercury-arc radiation. Kim and co-workers¹³ determined that the photodetachment threshold of ground-state HCO₂⁻ lies at 3.498(15) eV, consistent with earlier measurements.⁵¹ The photodetachment of anions trapped in solid neon generally requires photon energies that exceed the photodetachment threshold by 1 or 2 eV, in order to impart sufficient kinetic energy to the electron for it to avoid reattachment. A photodetachment threshold somewhat beyond 280 nm (4.4 eV) for HCO₂⁻ trapped in solid neon would be consistent with these observations. The product absorptions at 2455.7, 1628.9, 1626.4, 1323.0, and 744.1 cm⁻¹ grew somewhat in intensity when the sample was exposed to visible or near-ultraviolet radiation, but were destroyed when the sample was subjected to unfiltered mercury-arc radiation, appropriate for their contribution by HCO₂⁻.

Density functional calculations were conducted in order to obtain the isotopic substitution patterns for the vibrational fundamentals of HCO₂⁻. This information is especially helpful in resolving the disparity in the position of the CH-stretching mode. The structures obtained for HCO₂⁻ in these and other calculations are summarized in Table E-8 of Ref. 26. The experimental value of the CH bond length is rela-

TABLE III. Absorptions (cm⁻¹) assigned to HCO₂⁻ and DCO₂⁻.

Species	Sym.	Vib.	Na ⁺ H(D)CO ₂ ^{-a}	CEPA-1 ^b (Anharm.)	Ne matrix ^c
HCO ₂ ⁻	a ₁	1	2830	2447	2455.7
		2	1361	1293	1323.0
		3	775	710	744.1
	b ₂	4	1068	972	
		5	1607	1601	1628.9
		6	1367	1322	1626.4
DCO ₂ ⁻	a ₁	1	2131	1834	1844.6 ^d
		2	1331	1281	1309.1
		3	767	706	736.9
	b ₂	4	915	847	
		5	1589	1597	1625.0
		6	1013	977	1622.5

^aReference 12.

^bReference 11.

^cThis work. Based on previous investigations, the standard uncertainty (Type B) in the frequency measurement is ±0.1 cm⁻¹ (coverage factor, *k* = 1; i.e., 1σ).

^dReference 45.

tively uncertain. Although most of the observed structural parameters given in Table E-8 are from the x-ray diffraction study by Markila and co-workers,⁵² such studies have difficulty in determining parameters associated with H atoms. The value of 1.087(4) Å given in Table E-8 resulted from a neutron diffraction study of lithium formate monohydrate.⁵³ Kidd and Mantsch used a correlation between the frequency of the CH-stretching fundamental and the CH bond length to estimate a value of 1.11 Å. The CH bond lengths calculated for HCO₂⁻ are consistently greater than that estimate.

Correspondingly, the calculated CH-stretching frequencies of HCO₂⁻ summarized in Table E-9 of Ref. 26 are appreciably smaller than the value reported by Kidd and Mantsch.¹² The value obtained in the most sophisticated calculation, CEPA-1, including the anharmonic correction, differs from the neon-matrix absorption at 2455.7 cm⁻¹ by less than 9 cm⁻¹. A comparison of the values for the CEPA-1 harmonic and anharmonic calculations suggests that much of the disparity between the neon-matrix value and the values obtained in the other *ab initio* and density functional calculations results from neglect of the anharmonic correction. Because of spectral overlap with the prominent, structured absorptions of *trans*-HOCO and *trans*-DOCO, it was not possible to discern the CD-stretching absorption of DCO₂⁻ in the experiments on HCOOH-*d_n* samples. However, in the Ne:D₂:CO₂ experiments⁴⁵ it was identified at 1844.6 cm⁻¹, in excellent agreement with the value of 1834 cm⁻¹ obtained in the anharmonic CEPA-1 calculation.¹¹ The correspondence of the positions of the observed absorptions with the values obtained by Botschwina¹¹ in his CEPA-1 calculations of the anharmonic fundamentals of HCO₂⁻ and DCO₂⁻, given in Table III and, in a more detailed comparison, in Table E-9 of Ref. 26 is very satisfactory. Except for ν₁, the CH-stretching (or CD-stretching) vibration, the agreement with the infrared absorptions reported by Kidd and

Mantsch¹² for polycrystalline sodium formate is also satisfactory.

The observed positions for the vibrational fundamentals of the various heavy-atom isotopomers of HCO_2^- also correspond well with the calculated positions summarized in Table E-9 of Ref. 26. It would be difficult to find a combination band that could account for the 5 cm^{-1} observed shift in the 2455.7 cm^{-1} absorption in the $\text{Ne:H}^{13}\text{COOH}$ experiment. However, the assignment of this absorption to the CH-stretching fundamental accounts for it easily. The general pattern of isotopic shifts for the CH(D)-stretching fundamental agrees reasonably well with the calculated shifts, but most of the observed shifts are greater than the calculated shifts. The isotopic shifts for the other three observed fundamental absorptions, all of which involve principally the CO_2 moiety, track the calculated shifts closely. The two unassigned fundamental absorptions of HCO_2^- are calculated to have relatively low absorption intensities.

In summary, the assignments proposed in Table III for HCO_2^- and DCO_2^- are strongly supported by all of the experimental data and theoretical calculations. There appear to be two ways of accounting for the 2830 cm^{-1} absorption and for its counterpart in the deuterium substitution studies of Kidd and Mantsch.¹² These absorptions may arise from combination bands. However, there was no absorption near 2830 cm^{-1} in the present experiments. Alternatively, the electronic structure of the formate anion may be appreciably perturbed by the nearby sodium cation. Strong metal cation–anion interactions occur for several other anions, including CO_2^{18} and SO_2^{54} . For both of these anions, the antisymmetric stretching fundamental is lowered by approximately 50 cm^{-1} because of interaction with a metal cation.

IV. CONCLUSIONS

The most prominent product infrared absorptions in the experiments on normal and isotopically substituted Ne:HCOOH samples that are codeposited with microwave-excited neon atoms are contributed by *trans*-HOCO, *trans*-HCOOH⁺, and HCO_2^- . Five of the vibrational fundamentals of *trans*-HOCO were identified. Four vibrational fundamentals of *trans*-HCOOH⁺ were identified—three of them for the first time—with the help of density functional calculations of the isotopic substitution pattern for that species. In addition, four vibrational fundamentals of HCO_2^- were identified. The proposed assignments are supported by the results of detailed isotopic substitution studies. As predicted by CEPA-1 and other *ab initio* and density functional calculations, the CH-stretching fundamental of HCO_2^- is anomalously low in frequency. Density functional calculations were also conducted for the W-shaped dihydroxymethylene cation structure. Although that species may have been stabilized in the experiments, a definitive assignment was not possible. Additional density functional calculations were conducted to predict the structure and infrared spectrum of HCOOH^- . Infrared absorptions of HCOOH^- were not identified.

ACKNOWLEDGMENT

We wish to thank Dr. Karl K. Irikura for sharing with us the results of his calculations of the structure and vibrational fundamentals of HCO_2^- and DCO_2^- at the CCSD and CCSD(T) levels.

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