(8) As to the bishomoallyl interacting system, the lone pair orientations in 7-azanorbornene derivatives have also been studied: I. Morishima, K. Yoshikawa, K. Toyoda, K. Bekki, to be submitted for publication.

(9) The π participation effect on the rate of carbonium ion reaction in 2-bicyclo[2.2.2]oct-5-enyl structure has been appreciated: A. Lebel, J. E. Huber, Abstract of the 144th National Meeting of the American Chemical Society, March–April 1963, Los Angeles, Calif., 52M.

(10) M. P. Cava, C. K. Wilkins, Jr., D. R. Dalton, and K. Bessho, *J. Org. Chem.*, **30**, 3772 (1965).

(11) (a) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967); (b) J. B. Grutaner, M. Jautelet, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).

(12) (a) I. Morishima, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **92**, 6651 (1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *Chem. Commun.*, 1535 (1970); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **93**, 3922 (1971); (d) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, **94**, 1425 (1972).

(13) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1311 (1963); R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 5350 (1965).

(14) (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Am. Chem. Soc.*, **92**, 1267 (1970); (b) I. Morishima, K. Okada, and T. Yonezawa, *Chem. Commun.*, 33 (1971); (c) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, **54**, 3238 (1971); (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Jpn.*, **43**, 379 (1970).

(15) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1967).

(16) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(17) K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

(18) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Am. Chem. Soc.*, **89**, 3761 (1967).

(19) S. F. Nelsen, P. J. Hintz, and R. T. Landis, II, *J. Am. Chem. Soc.*, **94**, 7105 (1972).

(20) The ESR hyperfine coupling constant of 2-bicyclo[2.2.2]oct-5-enyl radical has been reported.[21] However, due to the planar structure around the radical center in this radical, these splitting constants do not correspond to the feature of the $Ni(AA)_2$-induced ^1H contact shifts of 2-azabicyclo[2.2.2]oct-5-enes.

(21) L. Bonazzola and R. Max, *Mol. Phys.*, **19**, 405, 899 (1970).

(22) The sizable contribution of contact shift to the $Eu(DPM)_3$-induced paramagnetic shift could also lead to misleading conclusions concerning the lone pair orientation.

(23) T. Yonezawa, I. Morishima, and K. Fukuta, *Bull. Chem. Soc. Jpn.*, **41**, 2297 (1968).

(24) The detailed study concerning the geometries of various bicyclic amines with minimization of calculated total energies will appear in a separate paper.

Raman Spectra of Alkali Metal–Iodine Matrix Reaction Products. Resonance Raman Spectrum of the Iodine Molecular Anion, I_2^-

Wilmont F. Howard, Jr., and Lester Andrews*

Contribution from the Chemistry Department, University of Virginia, Charlottesville, Virginia 22901.

Received August 21, 1974

Abstract: Argon matrix reactions of iodine ($Ar:I_2 = 500:1$) and alkali metal atoms have been examined by Raman spectroscopy. Excitation with the red line from a krypton ion laser has yielded a resonance Raman progression for each of the five alkali metal $M^+I_2^-$ species. Each series consisted of five or six members which decreased regularly in intensity and increased steadily in half-width. Statistical analysis gave the harmonic and first-order anharmonic frequencies and an estimate of the dissociation energy of I_2^-.

This study, the third in a series involving alkali metal-halogen reaction intermediates, was prompted by our earlier successes with $M^+F_2^-$ and $M^+Cl_2^-$.[1,2] Person estimated properties of I_2^- in 1963,[3] and the anion has been prepared by several routes and identified by electron spin resonance spectroscopy since then. For example, Zvi et al.[4] detected I_2^- in the ESR spectrum of 2537 Å photolyzed LiI glass at 77°K. Porret and Rossel[5] studied γ-irradiated CsI held at 100°K or less, and from the ESR spectrum of the crystal assigned a stability limit of 87°K to I_2^-. Lastly, Symons and Marov[6] bombarded 77°K aqueous solutions of alkali iodides with γ-rays and attributed subsequent ESR signals to the iodine molecular anion. Since the low-temperature matrix lends stability to otherwise elusive molecules, the study of I_2 matrix reactions with alkali metals was undertaken in search of the $M^+I_2^-$ species.

Experimental Section

The experimental technique, spectroscopic equipment, and cryogenic assembly have been previously described.[7,8] Iodine crystals (Mallinckrodt, Analytical Reagent) were held in a glass finger, and the vapor was allowed to reach equilibrium pressure (0.25 Torr)[9] in a 2-l. stainless steel sample can, after which sufficient Ar diluent was added to attain an $Ar:I_2$ ratio of 500:1. The gaseous sample was condensed on a tilted copper wedge maintained at 12°K at a spray-on rate of 2–3 mmol/hr. An atomic beam of alkali metal was simultaneously directed at the substrate, with metal vapor pressures of approximately 1 μ.[10] Raman spectra were recorded at 20 cm^{-1}/min from 50 to 800 cm^{-1} on a Spex Ramalog, using 500 μ slits and 6471, 5682, and 5309 Å excitation from a Coherent Radiation krypton plasma laser. Dielectric filters were employed to eliminate unwanted plasma emission lines; laser power was 200 mW at the sample with 6471 Å light, 100 mW with 5682 Å, and 150 mW with 5309 Å.

Calibration of the 6471 Å Raman spectra was done relative to the laser line. In order to provide a check, band separation in the progressions was plotted versus quantum number. The intercept gave the fundamental and the overtone wavenumbers were obtained by addition of the observed spacings. Wavenumber accuracy is ±1 cm^{-1}.

Results

Laser Raman spectra of matrix-isolated iodine species have been studied extensively.[11] Two resonance Raman progressions were observed using 5145 Å excitation, one originating at 212 cm^{-1} which was attributed to matrix-isolated I_2 monomer and another starting at 180 cm^{-1} which was assigned to aggregated I_2. The latter series was favored at higher iodine concentrations. Several of the resonance Raman bands of $(I_2)_n$ were observed here; however, the I_2 monomer species, which was much weaker with red excitation, was not detected in the present study.

A typical 6471 Å excited Raman spectrum following the addition of alkali metal atoms to the I_2 matrix sample is shown in Figure 1 for the $K + I_2$ reaction. The intense fundamental shifted near 114 cm^{-1} and four or five overtones with rapidly decreasing intensities were observed for all of the alkali metal reactions; Table I lists the wavenumber

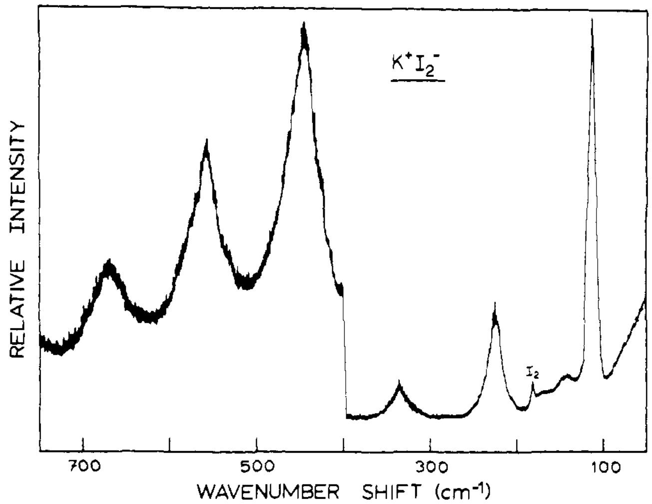

Figure 1. Resonance Raman spectrum of $K^+I_2^-$ at high dilution in solid argon at 12°K. Instrumental parameters: 200 mW of 6471 Å light at the sample; amplification ranges, right to left 30 and 0.3 × 10^{-9} A; 1 sec rise time; 20 cm^{-1}/min scan speed.

Table I. Wavenumber Shifts (cm^{-1}) of the Resonance Raman Bands of I_2^- in the $M^+I_2^-$ Species, with Half-Band Widths Shown Parenthetically, and the First Overtone/Fundamental Intensity Ratios ($2\nu/\nu$) using 6471 Å Excitation

Vibrational quantum no.	$Li^+I_2^-$	$Na^+I_2^-$	$K^+I_2^-$	$Rb^+I_2^-$	$Cs^+I_2^-$
1	115 (8)	114 (10)	113 (10)	116 (11)	115 (8)
2	228 (12)	226 (18)	226 (17)	232 (14)	230 (11)
3	341 (17)	338 (23)	337 (24)	347 (19)	343 (15)
4	453 (23)	448 (30)	447 (31)	461 (22)	457 (17)
5	564 (28)	558 (39)	556 (34)	574 (27)	570 (22)
6	674 (32)	666 (44)	664 (37)		682 (25)
($2\nu/\nu$)	0.28	0.26	0.28	0.38	0.40

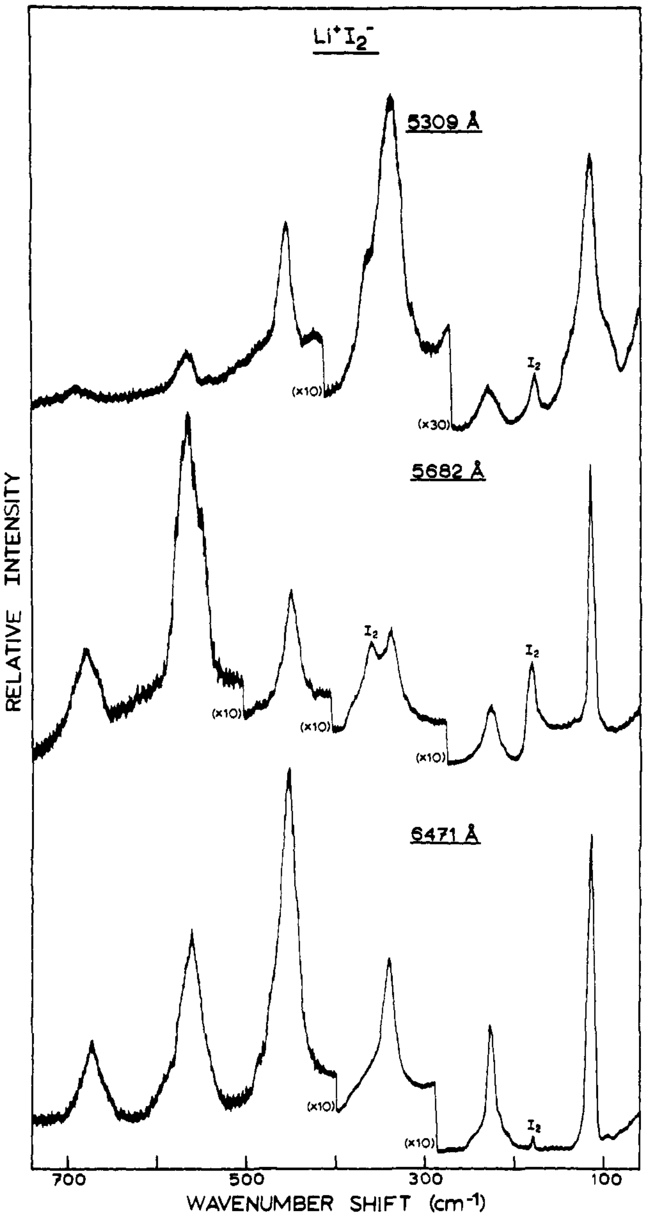

Figure 2. Exciting wavelength contrast for resonance Raman spectra of $Li^+I_2^-$. Instrumental parameters: 6471 Å, 200 mW power at the sample; 5682 Å, 100 mW; 5309 Å, 125 mW; ranges vary from 100 to 0.1 × 10^{-9} A going right to left; 1 sec rise time; 20 cm^{-1}/min scan speed. Parenthetic values denote amplification range changes.

data. Notice the small alkali metal effect on the fundamental and overtone wavenumbers which decreases Li-Na-K then increased for Rb and Cs. Intensity ratios (first overtone/fundamental) based on band height using 6471 Å excitation are also given in Table I.

The effect of exciting wavelength is contrasted in Figure 2 for the lithium-iodine reaction. The heavier metal-iodine species produced only a weak fundamental using the krypton yellow and green lines. As can be seen from the figure, the first overtone intensity relative to the fundamental decreased when the exciting wavelength was changed from 6471 to 5682 or 5309 Å. The higher overtone intensity also decreased with decreasing exciting wavelength as can be seen from Figure 2 keeping the amplification range changes in mind. $2\nu/\nu$ intensity ratios for the Li-I_2 species were 0.28, 0.15, and 0.13 for the three krypton exciting lines, respectively. Note also that the Raman spectra are extraordinarily intense.

The regularly increasing half-widths of the signals with increasing vibrational quantum number are shown in the figures; band half-widths using 6471 Å excitation are listed in Table I and are plotted versus vibrational quantum number in Figure 3.

Sodium reaction products in an experiment using Ar:I_2 = 300:1 were examined with argon ion laser lines. Excitation at 5145 Å revealed an intense I_2 aggregate[11] band at 180 ± 1 cm^{-1} and a weak feature at 112 ± 3 cm^{-1}. The 4880 Å laser line produced the intense 180 cm^{-1} I_2 fundamental and a weak band at 114 ± 3 cm^{-1}. The indigo exciting line at 4579 Å gave the strong I_2 signal at 180 cm^{-1} (7 cm^{-1} half-width) and a stronger, slightly broader signal at 112 ± 2 cm^{-1} (11 cm^{-1} half-width).

An experiment depositing K atoms into an Ar:I_2 = 300:1 sample was examined with 3564 Å krypton ion laser excitation. A broad (22 cm^{-1} half-width), moderately intense Raman band was observed Stokes shifted 109 ± 2 cm^{-1}; the longer wavelength regions revealed only plasma emission lines.

Several Raman experiments with condensed Ar:Br_2 mixtures (M:R = 75 to 200) and various alkali metals revealed a moderate signal at 295 ± 2 cm^{-1}, consistent with aggregated Br_2,[11] and a weak band at 162 ± 4 cm^{-1}. This latter signal showed no intensity enhancement with laser excitation ranging from 4579 to 6471 Å.

Discussion

The new vibrational progressions observed with red excitation when alkali metal atoms were codeposited with io-

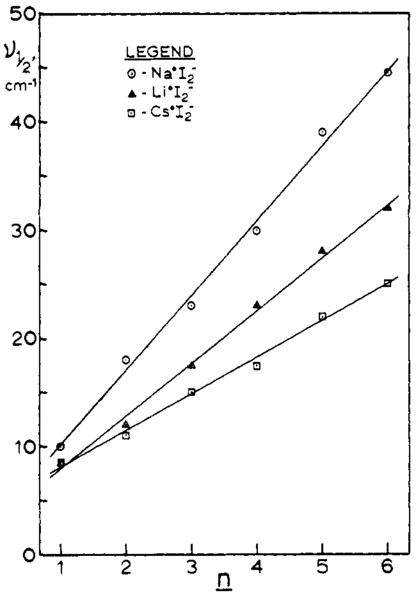

Figure 3. Plots of band half-width versus vibrational quantum number for three $M^+I_2^-$ species. Plots of $Rb^+I_2^-$ and $K^+I_2^-$ are intermediate to those shown and were omitted for clarity; half-width from 6471 Å excitation spectra.

dine show the regularly decreasing intensity pattern with increasing vibrational quantum number, which is characteristic of resonance Raman spectra.[12,13] The increase in band half-width with higher members of the series is often observed in the resonance Raman spectrum.[14] The maximum overtone intensity was found for 6471 Å excitation which indicates that the scattering species has a red absorption band.

$$M + I_2 \rightarrow M^+I_2^- \quad (1)$$

The appearance of the new resonance Raman progression following alkali metal reactions is indicative of charge-transfer reactions 1, like those proposed earlier for the $M^+F_2^-$ and $M^+Cl_2^-$ species.[1,2] Before assigning the spectra to $M^+I_2^-$, the unusually stable $M^+I_3^-$ species must be considered. The triiodide ion has a strong absorption at 3600 Å which tails off into the blue visible region[15] and causes the deep red color of I_3^- solutions. Accordingly, resonance Raman spectra of I_3^- have been observed in methanol solution using 3638 Å ultraviolet laser excitation which produced a 111 cm^{-1} fundamental and a five-membered overtone progression; preresonance Raman spectra of I_3^- have been observed with the 5145, 4880, and 4579 Å argon ion laser lines.[15] The vibrational energy per quantum, $\nu(n)/(n)$, increased from 111 to 114 cm^{-1} throughout the I_3^- overtone progression; this is indicative of a positive anharmonic term which may be present for a linear species. The Raman bands observed at 109 ± 2 cm^{-1} with 3564 Å excitation in the potassium-iodine matrix experiment and at 112 cm^{-1} with 4579 Å excitation in the Na-I_2 experiment could be due to the ν_1 mode of I_3^- in the matrix-isolated $M^+I_3^-$ species; the relatively high intensity of this Raman band and its increase in intensity with decreasing wavelength for the argon ion green and blue exciting lines indicates resonance enhancement. The $M^+I_3^-$ species can be synthesized by the following reactions on the sample surface during reagent condensation; reaction 3 represents the solution synthesis of I_3^-.

$$M + I_2 \rightarrow M^+I^- + I \quad (2)$$

$$M^+I^- + I_2 \rightarrow M^+I_3^- \quad (3)$$

The very intense fundamental and overtone progressions observed in this matrix-isolation study using 6471 Å excitation differ markedly from the I_3^- spectrum[15] in the exciting wavelength required for resonance Raman observation and the sense of the anharmonicity in the vibrational progression. All of the observations are consistent with the assignment of the red excited matrix spectrum to a resonance Raman progression in the ν_1 intraionic (I-I)$^-$ vibration of the $M^+I_2^-$ species.

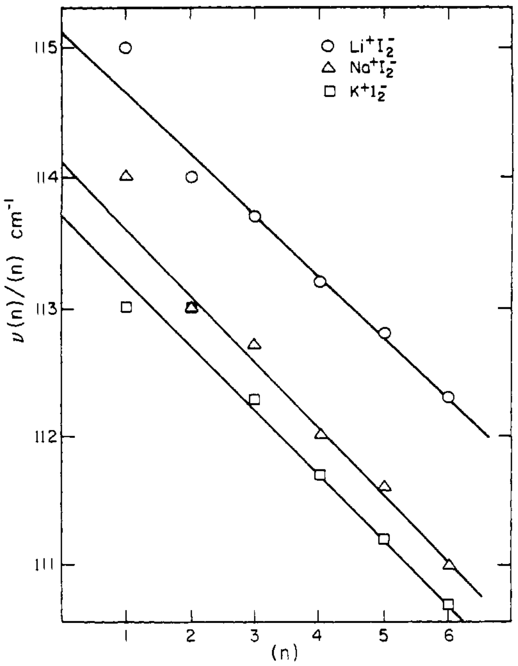

Figure 4. Plot of $\nu(n)/(n)$ versus (n), the vibrational quantum number, for three $M^+I_2^-$ species.

Table II. Harmonic and Anharmonic Vibrational Constants Obtained from Figure 4 and Dissociation Energies of I_2^- in the $M^+I_2^-$ Species Estimated from These Constants

	$Li^+I_2^-$	$Na^+I_2^-$	$K^+I_2^-$
ω_e, cm^{-1}	115.6	114.6	114.2
$\omega_e x_e$, cm^{-1}	0.47	0.50	0.50
D_e, kcal/mol	21	20	18

Variation in the fundamental wavenumbers for I_2^- reflects the metal effect on ν_1, the intraionic mode. The $M^+I_2^-$ species has two symmetric stretching modes, the ν_1 intraionic mode and the ν_2 interionic ($M^+ \leftrightarrow I_2^-$). As the weight of M increases, ν_2 decreases approaching ν_1, and forces ν_1 to lower wavenumbers by interaction between modes of like symmetry, which is the case for the Li, Na, and K species. The cross-over for ν_2 occurs with $Rb^+I_2^-$. The harmonic gas phase RbI frequency[16] is 138 cm^{-1} which, accounting for anharmonicity and matrix shift, implies an argon matrix value near 125 cm^{-1}. Owing to the appearance of ν_2 of $Li^+Cl_2^-$ below LiCl in the spectrum,[2] the ν_2 mode for $Rb^+I_2^-$ is estimated at 100-110 cm^{-1}. If ν_2 of $Rb^+I_2^-$ appears at this position, the deviation for the rubidium species can be explained by the vibrational interaction.

The standard treatment[2,13] of bands in a vibrational progression involves plots of $\nu(n)/(n)$ vs. (n), which are illustrated in Figure 4 for three alkali metal I_2^- progressions. Notice the very good straight-line graphs. Values of ω_e and $\omega_e x_e$ obtained from the plots are listed in Table II along with calculated upper limits to the I_2^- dissociation energy.

The harmonic I_2^- wavenumbers, near 115 cm^{-1} depending upon the cation, are about 100 cm^{-1} less than matrix isolated I_2 at 212 cm^{-1} whereas the anharmonic constants for I_2^- are only slightly less than the 0.52 cm^{-1} I_2 matrix value.[11] As was found for F_2^- and Cl_2^-, the I_2^- fundamental at 115 cm^{-1} is roughly half of the precursor I_2 frequency. The electron transferred from the alkali metal enters an antibonding molecular orbital on iodine and reduces the σ bond order from one to one-half, a bonding change which is in line with the change in fundamental frequency upon reduction of molecular iodine.

The dissociation energies calculated for I_2^- from the ω_e and $\omega_e x_e$ values listed in Table II average 20 kcal/mol. The average value is in reasonable agreement with the thermodynamic value, 24.5 ± 2 kcal/mol, obtained from the following Hess' law calculation, which supports the present spectroscopic analysis and observation of I_2^-.

$$\begin{array}{ll}
I_2^- \longrightarrow I_2 + e^- & 59.5 \pm 2\ \text{kcal/mol}^{17} \\
I_2 \longrightarrow 2I & 33.57 \pm 0.03\ \text{kcal/mol}^{18} \\
I + e^- \longrightarrow I^- & -70.6 \pm 0.1\ \text{kcal/mol}^{19} \\
\hline
I_2^- \longrightarrow I + I^- & 24.5 \pm 2\ \text{kcal/mol}
\end{array}$$

The regularly increasing half-band widths noted here for the resonance Raman progression of I_2^- are typical of solution spectra,[14,20] but this increase was not observed[2] for Cl_2^-, although a slight increase was found for matrix isolated O_3^- and ClO_2.[21,12] The increase in band width for I_2^- was linear with quantum number as illustrated by Figure 3. A reasonably linear plot was found for dissolved I_2 from the second to thirteenth overtones.[14] The band broadening in the solid phase may be due to a guest-host interaction, which is stronger for the more polarizable $M^+I_2^-$ species than for $M^+Cl_2^-$.

The weak Raman bands observed near 162 cm^{-1} in alkali metal-bromine experiments could be due to either Br_2^- or Br_3^-. The latter reddish species[22] has been observed at 162 cm^{-1} in Raman spectra of chloroform solutions of $R_4N^+Br_3^-$ and the former species could reasonably be predicted at half of the Br_2 fundamental, which suggests a band near 160 cm^{-1} for Br_2^-. By analogy with the Cl_2 and I_2 alkali metal studies, the $M^+Br_2^-$ species was probably produced in small quantities from the matrix reaction.

Conclusions

The resonance Raman spectrum of I_2^- has been observed in solid argon for all of the alkali $M^+I_2^-$ species using krypton ion 6471 Å excitation; the $Li^+I_2^-$ species was also observed with 5682 and 5309 Å illumination. The six-membered vibrational progressions beginning near 115 cm^{-1} decreased in intensity and increased in band width in a regular manner with increasing vibrational quantum number. The potassium-iodine reaction products were examined with 3564 Å excitation; an intense 109 cm^{-1} fundamental was observed and presumed to be due to I_3^-, which is not to be confused with the I_2^- fundamentals near 115 cm^{-1} depending upon alkali cation, which required red excitation for resonance Raman observation.

Acknowledgment. The authors gratefully acknowledge financial support for this research by the National Science Foundation under Grant GP-38420X and an Alfred P. Sloan Fellowship for L.A.

References and Notes

(1) W. F. Howard, Jr., and L. Andrews, *J. Am. Chem. Soc.*, **95**, 3045 (1973); *Inorg. Chem.*, 14, 409 (1975).
(2) W. F. Howard, Jr., and L. Andrews, *J. Am. Chem. Soc.*, **95**, 2056 (1973); *Inorg. Chem.*, **14**, 767 (1975).
(3) W. B. Person, *J. Chem. Phys.*, **38**, 109 (1963).
(4) E. B. Zvi, R. A. Beaudet, and W. K. Wilmarth, *J. Chem. Phys.*, **51**, 4166 (1969).
(5) F. Porret and J. Rossel, *Helv. Phys. Acta*, **42**, 191 (1969).
(6) M. C. Symons and I. N. Marov, *J. Chem. Soc. A*, **1**, 201 (1971).
(7) D. A. Hatzenbühler and L. Andrews, *J. Chem. Phys.*, **56**, 3398 (1972).
(8) L. Andrews, *J. Chem. Phys.*, **57**, 51 (1972).
(9) S. I. Sklyarenko, B. I. Markin, and L. B. Belyaeva, *Zh. Fiz. Khim.*, **32**, 1916 (1958).
(10) D. E. Tevault and L. Andrews, *J. Phys. Chem.*, 77, 1646 (1973).
(11) W. F. Howard, Jr., and L. Andrews, *J. Raman Spectrosc.*, **2**, 447 (1974).
(12) F. K. Chi and L. Andrews, *J. Mol. Spectrosc.*, **22**, 82 (1974).
(13) W. Kiefer and H. J. Bernstein, *Mol. Phys.*, **23**, 835 (1972).
(14) W. Kiefer and H. J. Bernstein, *J. Raman Spectrosc.*, **1**, 417 (1973).
(15) W. Kiefer and H. J. Bernstein, *Chem. Phys. Lett.*, **16**, 5 (1972); W. Kiefer, *Appl. Spectrosc.*, **28**, 115 (1974).
(16) J. R. Rusk and W. Gordy, *Phys. Rev.*, 127, 817 (1962).
(17) W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, **55**, 2724 (1971).
(18) R. J. LeRoy and R. B. Bernstein, *Chem. Phys. Lett.*, **5**, 42 (1970).
(19) R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1546 (1963).
(20) W. Kiefer and H. J. Bernstein, *J. Mol. Spectrosc.*, **43**, 366 (1972).
(21) L. Andrews and R. C. Spiker, Jr., *J. Chem. Phys.*, **59**, 1863 (1973).
(22) W. B. Person, G. R. Anderson, J. N. Fordemwalt, H. Stammreich, and R. Forneris, *J. Chem. Phys.*, 35, 908 (1961).

+*E* Collision Induced Mass Spectra from Negative Ions

J. H. Bowie* and T. Blumenthal

Contribution from the Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia, 5001. *Received August 30, 1974*

Abstract: A new type of mass spectrum is described in which negative ions are converted into decomposing positive ions in the analyzer region of the mass spectrometer. Initial results suggest that these spectra may provide information concerning the structures of both negatively and positively charged ions.

Beynon, Cooks and colleagues have described the application of high-energy ion-molecule reactions occurring in the analyzer regions of the mass spectrometer to effect charge stripping[1] and charge exchange reactions.[2] Such reactions provide information concerning both the structures and fragmentations of ions[1-3] and the energy characteristics and reaction mechanisms of ion-molecule reactions at high energy.[1,2,4] As an extension to this work, Keough, Beynon, and Cooks have reported[5] that particular positively charged ions may be converted to the corresponding negative ions by the collision process

$$M^+ + N \rightarrow M^- + N^{2+}$$

where N is the target gas, generally maintained at a pres-