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# Dimethyl-diacetylene radical cation and its fluorescence spectra in rare gas matrices

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Matrix spectra of the  $C_6H_6^+$  species in solid Ne exhibit a well resolved vibrational structure, which shows a remarkably good agreement with the gas phase fluorescence. The ions in solid Ar are more strongly perturbed and show an interesting line shape asymmetry between the emission and excitation spectra. These are discussed in terms of the ion-host interaction potentials.

## INTRODUCTION

The field of ion electronic spectroscopy has been expanding rapidly in the recent years, and in particular the emission spectra of a variety of halogenated benzene radical cations<sup>1,2</sup> have been studied, mostly using electron impact ionization of the parent molecules. We have recently reported the laser fluorescence and excitation spectra of these species in the gas phase<sup>3</sup> and in solid argon.<sup>4</sup> These show a sharp and well resolved vibronic structure and remarkably little perturbation by the solid environment.

Substituted acetylenes are another class of compounds, whose cations are known to relax in the gas phase efficiently via the radiative channel. In fact, the first observed spectrum of a polyatomic ion belonged to this group. Schuler observed in 1951 a new spectrum in a discharge through a benzene-helium mixture,<sup>5,6</sup> and its carrier was later identified by Callomon as the diacetylene radical cation,<sup>7</sup>  $C_4H_2^+$ . Emission from several more ions belonging to this group<sup>8,9</sup> has recently been observed. Allan *et al.*<sup>8</sup> have reported emission from the dimethyl derivative. In the present work we examine the spectra of the dimethyldiacetylene radical cation in rare gas matrices using the laser excitation fluorescence technique. Studies of this kind are useful for several reasons. In the first place, the low temperature matrix studies provide new information about the spectroscopy of the guest ions. In addition, perhaps even more importantly, it gives insight into the interactions between the ion and the rare gas solvent.

## EXPERIMENTAL

A sample of the dimethyl-diacetylene was obtained from the Chemical Samples Company, and was used without purification. It was premixed with the matrix gas (Ar or Ne) in ratios of 1:2000–1:10 000 and deposited on a sapphire window at  $\sim 5^\circ K$ . The ions were prepared by photolysis *in situ* using a microwave discharge through a mixture of 10%  $H_2$  and 90% He. Typically 2–3 moles were deposited over 45–60 min and subsequently photolysed for 1–5 min.

A Hansch design  $N_2$  laser pumped dye laser of home built variety was used to excite the fluorescence. The emission was wavelength and time resolved and the signal processed by a minicomputer controlling the experiment.

## RESULTS AND DISCUSSION

### Neon matrix spectra and $C_6H_6^+$ vibronic structure

Laser irradiation of the unphotolyzed samples in the blue and near UV produced no visible emission. This is not surprising, since dimethyl-diacetylene does not absorb in this spectral range. Excitation of samples following a brief photolysis using the 10.2 eV Lyman- $\alpha$  radiation resulted in an intense green fluorescence. The emission spectrum obtained in a Ne matrix is shown in Fig. 1. It consists of an extensive system of sharp lines, each of them followed by a lower energy phonon sideband. The spectrum is independent of the wavelength of the excitation and the emission apparently oc-

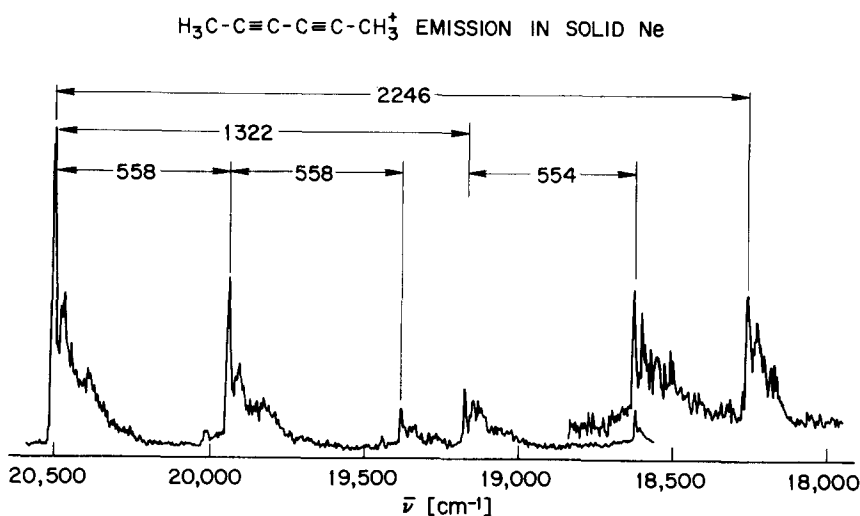


FIG. 1.  $CH_3-C\equiv C-C\equiv C-CH_3$  emission spectrum in solid Ne, with  $21\,030\text{ cm}^{-1}$  excitation.

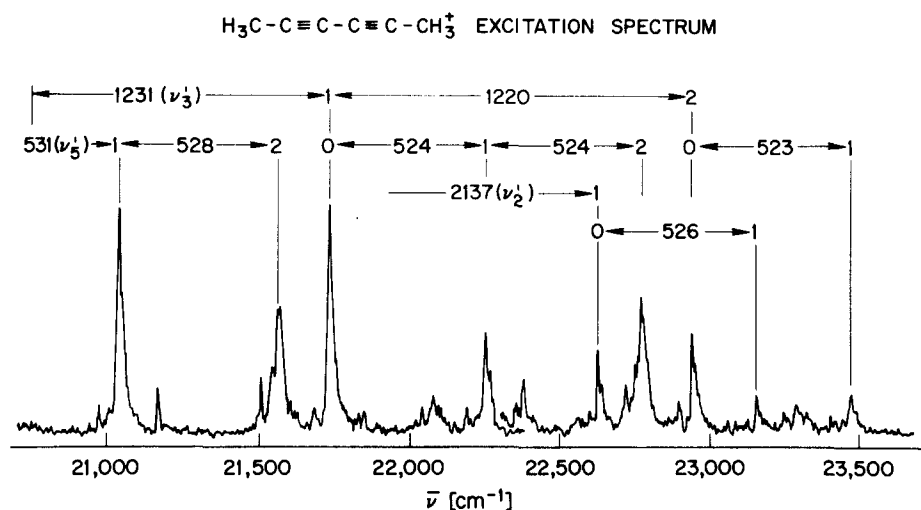


FIG. 2.  $\text{CH}_3-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_3^+$  excitation spectrum in solid Ne at 4°K. The 0-0 emission at 20 499  $\text{cm}^{-1}$  was monitored. The spectrum is not corrected for laser power variation.

curs from the vibrationless level of the excited electronic state. The highest energy band appears at 20 499  $\text{cm}^{-1}$  and is assigned to the electronic origin. The remaining sharp bands are then easily assigned to an array involving vibrational frequencies of 558, 1322, and 2246  $\text{cm}^{-1}$ .

Overall, the spectrum is remarkably similar to the gas phase emission observed by Allan *et al.*<sup>9</sup> and leaves little doubt that the dimethyl-diacetylene radical cation is the carrier. The spectrum undergoes a gas-matrix shift of  $\sim 63 \text{ cm}^{-1}$ . The observed frequencies are, assuming a  $D_{3d}$  symmetry for the ion, the  $a_{1g}$  modes  $\nu_5$  and  $\nu_4$ , the central C-C and end C-C stretch, and  $\nu_2$ —the C≡C symmetric stretch. Both the  $\nu_5$  and  $\nu_2$  reproduce the gas phase values within their stated accuracy of  $\pm 10 \text{ cm}^{-1}$ . A slight discrepancy exists only in the case of  $\nu_4$ , where a value of  $1300 \pm 10 \text{ cm}^{-1}$  was reported in the gas phase compared to the 1322  $\text{cm}^{-1}$  observed in the matrix. While it is a possibility that this shift is real and represents a matrix effect, it should be noted that the rotationally unresolved gas phase bands are usually relatively broad and the determination of the band origins is thus subject to some imprecision.

Matrix studies are particularly useful in providing information about the excited electronic states. This information is usually not available from the gas phase emission spectra, and only low accuracy data are obtained from photoelectron spectroscopy. Figure 2 shows a matrix excitation spectrum of the  $\text{C}_6\text{H}_6^+$  species in solid Ne. The origin band (not shown in the figure) occurs at 20 499  $\text{cm}^{-1}$ , coincident with the energy derived from the emission spectrum. The analysis of the strong features in the spectrum is quite analogous to that of the emission spectrum and gives values of 531, 1231, and 2137  $\text{cm}^{-1}$  for the  $\nu_5'$ ,  $\nu_4'$ , and  $\nu_2'$  modes in the upper state. The former two are within the experimental error of the results from the photoelectron spectra,  $520 \pm 40$  and  $1220 \pm 40$ , while the previously unreported  $\nu_2'$  is reasonably close to the parent  $\nu_2$  frequency (2254  $\text{cm}^{-1}$ ).<sup>10,11</sup>

It should be noted that the upper state 1231  $\text{cm}^{-1}$  frequency appears in the spectrum as the strongest pro-

gression forming mode, and, based on Franck-Condon type arguments, is clearly the counterpart of the 1322  $\text{cm}^{-1}$  mode which is the most prominent vibration in the emission spectrum. In the previous gas phase work, the latter frequency was assigned to  $\nu_3$ , which is predominantly the CH bending mode (1381  $\text{cm}^{-1}$  in the parent). Our results indicate that a consistent assignment for the two vibrations should be chosen. A study of deuterated samples would be necessary to provide an unambiguous answer, but we favor the  $\nu_4$  C-C stretching vibration assignment for both frequencies; the other two symmetric frequencies involving the C atom chain both appear strongly in the spectrum, and the appearance of the remaining one,  $\nu_4$ , can also be expected. The methyl groups are further removed from the chromophore, and the absence of the two methyl frequencies  $\nu_1$  and  $\nu_3$  should not be surprising.

In addition to the strong bands discussed above, numerous weaker, sharp bands appear in the excitation and, to a lesser extent, in the emission spectrum. These do not fit into the array of the totally symmetric vibrations, and one can advance several explanations for their origin. They could be totally symmetric combinations or overtones of the asymmetric vibrations, they could be nontotally symmetric fundamentals appearing due to lowering of the ion's symmetry due to the Jahn-Teller effect, or they could be medium induced. The entire spectrum undergoes a negligible gas-neon shift, and the assigned vibrational modes appear to be, where gas phase data are available, only insignificantly perturbed. Furthermore, there are very few clearly documented cases where the matrix modifies significantly the geometry of a strongly bound guest. It appears likely, that the weak bands appearing in the spectrum are, at least partly, intramolecular in origin.

The carbon atom chain in the dimethyl-diacetylene radical cation is expected to be linear, similar to the unsubstituted  $\text{C}_4\text{H}_2$ , and one can therefore discuss the transition to a good approximation in terms of  $D_{\infty h}$  symmetry and an  $A^2\Pi_u \rightarrow X^2\Pi_g$  transition. Both of the electronic states are doubly degenerate, and one might therefore speak about a Renner-Teller splitting, which

may be quite substantial, (Jahn–Teller splitting if one considers the methyl groups and the overall  $D_{3d}$  symmetry). The Renner–Teller splitting often makes the analysis of even triatomic spectra a nontrivial problem, and in the case of  $C_6H_6^+$  with several degenerate vibrations it could result in an extremely complex spectrum.

Attempts at detailed assignments of the weak bands with the present data would therefore not be very meaningful. Studies of the spectra at high resolution in the gas phase or matrix studies of isotopically enriched samples and of the unsubstituted diacetylene and monomethyl-diacetylene cations might give more detailed information.

A subject of some interest is the quantum yield of emission. Dannacher<sup>12</sup> has also studied the 2,4 hexadiyne radical cation using the photoelectron-photoion coincidence technique. From the relative abundance of the fragment ions, an upper limit for the quantum yield of 0.6 was deduced for the A–X fluorescence. In the matrix samples we observe no bleaching of the fluorescence signal. It would thus appear that the photodissociation is either suppressed in the matrix, or the fragments recombine with near unity quantum yield to reform the ground state cations. It is, however, possible that in the gas phase the fragmentation requires vibrational or rotational excitation.

#### Spectra in Ar matrix and guest-host interactions

The character of the spectra in Ar solid differs substantially from the Ne matrix spectra discussed above. Both the emission and excitation spectrum are presented in Fig. 3. The excitation spectrum shows a strong origin band near 20 190  $cm^{-1}$ . At higher energies the excited vibrational bands appear and can be analyzed in a way quite analogous to the Ne spectrum. All the bands are, however, rather broad with FWHM  $\sim 70\text{ }cm^{-1}$ . With linewidths of this magnitude, the vibrational fre-

quencies obtained are of course of lower accuracy. We get values of 518, 1220, and  $2118 \pm 10\text{ }cm^{-1}$  for the  $\nu'_5$ ,  $\nu'_4$ , and  $\nu'_2$  modes, respectively.

The linewidths seen in Fig. 3 are essentially homogeneous, that is, the positions of the bands do not depend on the exact wavelength whose intensity is measured. The asymmetric appearance of the bands suggests that the dominant contribution to the lineshapes is the homogeneous phonon contour. The emission, while too fast for accurate lifetime determination with our resolution, has an observable lifetime of  $\sim 10\text{ ns}$ . The fact that even the origin band is broad rules out the possibility that the widths are dominated by lifetime broadening.

The left hand side of Fig. 3 shows the  $C_6H_6^+$  emission spectrum. The bands in this spectrum are quite broad (FWHM  $\sim 350\text{--}400\text{ }cm^{-1}$ ) and incompletely resolved. The origin band does not coincide with the 0–0 band in the absorption–excitation spectrum, but the maximum is shifted some  $440\text{ }cm^{-1}$  from the first maximum in the excitation spectrum. While determination of the maxima positions for bands  $400\text{ }cm^{-1}$  wide is subject to large errors, one can estimate vibrational frequencies of  $\sim 520$  and  $1300\text{ }cm^{-1}$  from the emission. As in the excitation spectrum, the linewidth is apparently homogeneous.

Clearly, the appearance of the Ar matrix data raises two important questions. (a) Why do the Ar matrix spectra differ so drastically from the neon results? (b) Why are the phonon bandshapes in emission and in excitation quite different?

The electron affinity<sup>13</sup> of the dimethyl-diacetylene cation is  $\sim 9\text{ eV}$  and that of its excited state is larger by its excitation energy, while the ionization potential of neon is  $\sim 21\text{ eV}$ . The neon atoms with their low polarizability will therefore not interact strongly with the

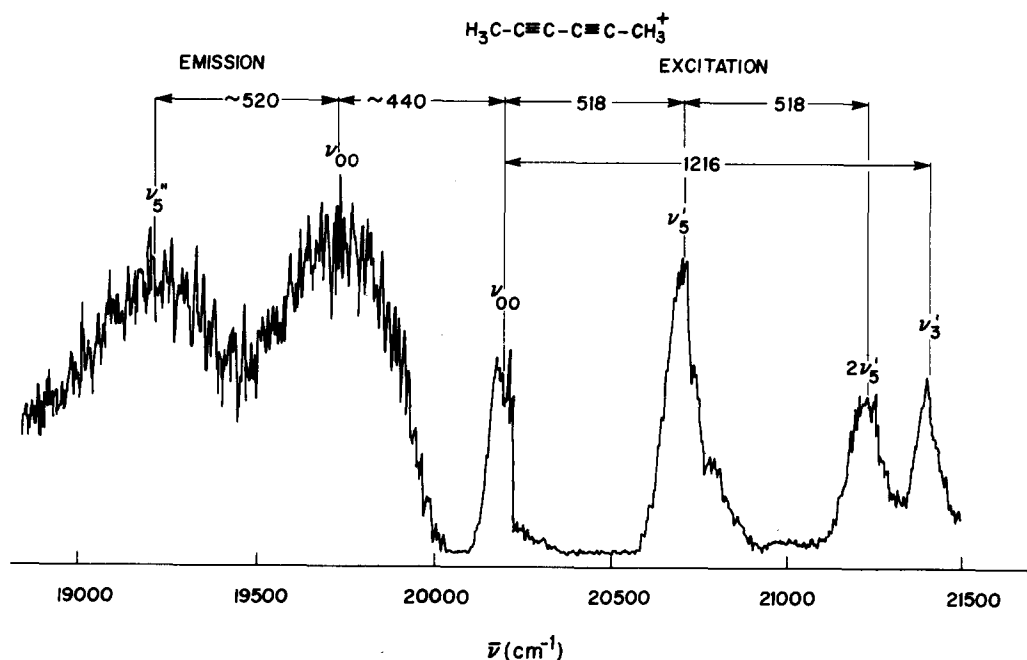


FIG. 3. Sections of the emission and excitation spectrum of  $C_6H_6^+$  in solid Ar in the neighborhood of the origin.

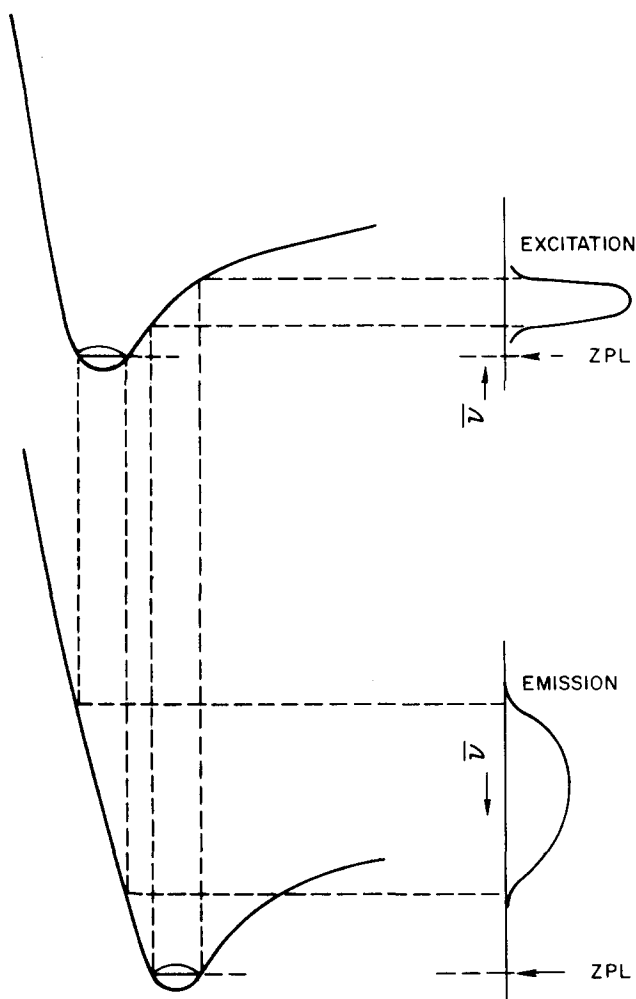


FIG. 4. Schematic diagram of the ion-lattice interaction potentials explaining the origin of the lineshapes observed in Ar matrix.

ionic guest and one can to a good approximation picture the system in the conventional way of only a weakly perturbed guest in an inert cage. The ionization potential of an Ar atom is on the other hand only  $\sim 15$  eV in the gas phase, and indubitably considerably lower in the solid environment. One can therefore imagine a charge transfer type interaction between the ionic guest and the Ar lattice atoms, who act as weak electron donors. This strong interaction results in changes of the electron density in the  $C_6H_6^+$  guest and in the rather strong perturbation of its vibrational frequencies.

One usually expects emission and excitation spectra associated with the same electronic transition to have similar phonon lineshapes. This can indeed be observed in the spectra of most matrix isolated molecules. It is the consequence of application of Franck-Condon factors to the lattice phonons, when the guest-host interaction is relatively weak and similar in magnitude in the initial and final state of the transition. Under these circumstances the phonon contour is controlled by the harmonic bottom of the potential well. If the interaction potentials in the initial and final state are grossly different and the potential minima occur at different equilibrium distance, the emission-absorption phonon bandshape sym-

metry will break down due to the anharmonicity of the interaction potential. This is shown schematically in Fig. 4, where potential curves represent, in one dimension, the guest-host interaction. In the example shown the interaction is stronger in the upper state and the minimum occurs at a shorter guest-host distance. Under these circumstances the absorption will be controlled by the flat outside portion of the potential and result in relatively sharp lines. The emission process will, on the other hand probe the steep inner limb corresponding to the hard-sphere repulsion and will result in the broad wing.

Physically, the absorption process occurring on the vertical transition will populate excited phonon levels in the upper state, and will be followed by fast relaxation and rearrangement of the solvent into the new equilibrium geometry. Subsequently, emission will again occur into excited phonon levels in the ground electronic state. A consequence of this model is a gap between the origin of the emission and excitation spectrum, as observed. The zero phonon line, corresponding to the adiabatic process connecting the fully relaxed geometries, which is strongly Franck-Condon forbidden, will be extremely weak and located between the origins of the emission and excitation spectra. In the present spectrum of  $C_6H_6^+$  in solid Ar it was not observed.

It is interesting to note that a similar but reversed case of phonon lineshape asymmetry has been recently observed<sup>14</sup> in the spectroscopy of the  $A^2\Sigma^+$  Rydberg state of NO. There the emission spectrum was relatively sharp and the excitation spectra extremely broad, and this was rationalized using a similar Franck-Condon argument, and the assumption of the formation of a spherical "bubble" around the excited Rydberg state.

Numerous infrared spectra of small cations in solid matrices were recently reported. Our results suggest that the best medium for the study of ionic spectra should be solid Ne. In solid Ar the vibrational frequencies may be rather strongly perturbed by the host matrix.

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