Chemical Physics AI

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Citation: J. Chem. Phys. 83, 6091 (1985); doi: 10.1063/1.449600 View online: http://dx.doi.org/10.1063/1.449600 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v83/i12 Published by the American Institute of Physics.

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Triplet state spectroscopy and photophysics of As₂ in solid neon

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(Received 8 July 1985; accepted 13 September 1985)

 As_2 dimer molecules generated by evaporating gallium arsenide were trapped and studied in solid neon. Components of at least three different excited electronic states are populated by direct tunable laser excitation and observed in phosphorescence. Nonradiative vibrational and electronic relaxation processes occurring in the matrix have been investigated. The electronic structure and spectroscopy of As_2 is reviewed and summarized.

I. INTRODUCTION

Properties and spectroscopy of metal dimers and other small clusters are areas of considerable current interest.^{1–5} This interest stems in part from the desire to characterize the properties of atoms on metal surfaces and to understand on a molecular level heterogeneous chemical catalysis and similar processes occurring on metal surfaces. One of the techniques which led to advances in this field in recent years and which helped to characterize numerous small metal clusters is matrix isolation.^{6–9} Studies in low-temperature matrices have helped to clarify the electronic structure of clusters of the heavy group Va metals,^{10–14} Sb and Bi and have also been useful in investigations of the nonmetallic, light group V elements N and P.¹⁵ The remaining group Va dimer, As₂, has been less extensively studied.

Arsenic is usually considered to be a nonmetallic element, but it possesses a metal-like modification which exhibits a high conductivity and other metallic properties. Molecular As₂ was first observed¹⁶ in 1934 and has been studied in the gas phase by several investigators.¹⁷⁻²⁴ Particularly extensive recent studies are due to d'Incan and Perdigon and their co-workers. Excited singlet states of As2 directly accessible from the $X^{1}\Sigma_{g}^{+}$ ground state dissociate into two excited As atoms and are therefore high in energy, above 40 000 cm^{-1} . The visible and near UV spectroscopy of As₂ is therefore limited mainly to excited triplet states. Matrix isolation spectroscopy often yields new insights and information not readily available in gas-phase studies. In particular, nonradiative transitions and relaxation processes often populate electronic states otherwise inaccessible in direct absorption experiments and thus permit studies of strongly forbidden transitions.^{22,23} Solid neon is a particularly suitable medium which yields relatively unperturbed, gas-phase-like spectra.

Vapors of many metals are predominantly monatomic and one therefore has to work with concentrated matrices, and use annealing or other techniques to ensure that observable concentrations of the dimers are stabilized. Quite the opposite problem is encountered with As and other group Va elements, whose vapors are predominantly tetratomic, and where very high temperatures are needed to generate appreciable dimer concentrations. Heating of group IIIb arsenides and phosphides provides convenient, low temperature sources of the As₂ and P₂ dimers which, in fact, have important potential applications in processes such as molecular beam epitaxy and related techniques for semiconductor growth.^{24–26} Matrices generated using such a source are investigated in this manuscript using time resolved, laser induced fluorescence. These studies provide new information about the spectroscopy and dynamics of As_2 molecules in solid rare gases.

II. EXPERIMENTAL

GaAs was used as a source of the As₂ molecules in the present study. The sample was placed in a quartz crucible and evaporated from a tungsten furnace, with temperatures in the range of 350–400 °C being needed to generate adequate As₂ concentrations. In several control experiments As₂ was produced by evaporating pure arsenic in a quartz capillary heated to ~1000 °C and dissociating the As₄ molecules.

In either case the metal vapor was co-deposited with the matrix gas on a metal substrate held at 4 K. Deposits thus formed over a period of 10–30 min were usually quite colorless or, in some cases, faintly yellow. While careful measurements of sample concentrations were not carried out, one can estimate from the amount of solid residue left on the substrate after matrix vaporization that the dilution was always higher than 1000:1. The samples were excited using a nitrogen laser pumped dye laser (Molectron DL14). The sample reemission was viewed either undispersed, or resolved in a Spex 14018 double monochromator. Photomultiplier signal was amplified, digitized in a waveform recorder (Biomation 8100), and averaged.

III. RESULTS AND DISCUSSION

A. Observed spectra

Excitation of matrix samples containing arsenic results in a rather extensive and strong emission. Depending on excitation wavelength, at least four distinct emission systems are observable, spanning the range from near infrared to UV. One of the emission band systems occurs in the near infrared and one in the yellow-green portion of the spectrum, with two additional systems being located in the blue between $21-24\ 000\ \mathrm{cm}^{-1}$.

Excitation of the sample below $\sim 19000 \text{ cm}^{-1}$ produces a long-lived near-infrared emission system, whose spectrum is shown in Fig. 1(a). It consists of a regular progression of sharp, instrumentally limited bands, with widths (FWHM) of less than 2 cm⁻¹. The spectrum abruptly ter-



FIG. 1. The $c^{3}\Sigma_{u}^{+}(1_{u}) \leftrightarrow X^{1}\Sigma_{g}^{+}$ system of As₂ in solid neon. (A) Emission; (B) section of the excitation spectrum. Note the absence of any maxima attributable to the 0_{u}^{-} component, expected near the frequencies marked by the arrows.

minates at the red end due to loss of sensitivity of our PMT beyond 9000 Å. The excitation spectrum of the phosphorescence, part of which is shown in Fig. 1(b), contains a similar progression with $\sim 300 \text{ cm}^{-1}$ spacing. Even though the intensity falls off rapidly at the low energy end, the correct vibrational assignments are readily established, since the first observed excitation band coincides exactly with the highest energy band observed in emission and is therefore clearly the 0–0 transition. A listing of the vibronic bands observed in the spectra is given in Table I, and their analysis leaves little doubt that As₂ in its lowest $c {}^{3}\Sigma_{u}^{+}$ state is the emitter.

When excitation of the sample occurs at energies above $\sim 20\ 000\ \mathrm{cm}^{-1}$ a new emission appears in the yellow region which, unlike the sharp $c\ ^{3}\Sigma_{u}^{+}$ state phosphorescence contains a progression of broad features. Under higher resolution each band exhibits a sharp zero-phonon line and an

TABLE I. Vibronic bands in the red spectrum of As₂ in solid Ne^{*} $c^{3}\Sigma_{u}^{+}(1_{u}) \leftrightarrow S^{1}\Sigma_{g}^{+}$.

| Emission ^b | | Excitation | | | | |
|-----------------------|-------------|------------|-------------|----|-------------|--|
| v" | $\bar{\nu}$ | v' | $\bar{\nu}$ | v' | $\bar{\nu}$ | |
| 0 | 14 440 | 0 | 14 440 | 17 | | |
| 1 | 14 012 | 1 | | 18 | 19 737 | |
| 2 | 13 586 | 2 | 15 060 | 19 | 20 010 | |
| 3 | 13 164 | 3 | 15 368 | 20 | 20 282 | |
| 4 | 12 744 | 4 | 15 674 | 21 | | |
| 5 | 12 324 | 5 | 15 980 | 22 | 20 819 | |
| 6 | 11 908 | 6 | 16 282 | 23 | 21 085 | |
| 7 | 11 494 | 7 | | 24 | | |
| 8 | 11 080 | 8 | | | | |

* All values in cm⁻¹; wave numbers accurate to ± 2 cm⁻¹.

^b All emission bands originate from the vibrationless v' = 0 level; similarly the excitation spectrum show only vibronic bands with v'' = 0.



FIG. 2. Spectra assigned to the $e^{3}\Delta_{u} \leftrightarrow X^{1}\Sigma_{g}^{+}$ system of As₂ in solid neon (see the text). (A) Two of the broad emission bands attributed to the $e^{3}\Delta_{u}(2_{u})$ component; (B) two bands of the corresponding excitation spectrum, due to the $e^{3}\Delta_{u}(1_{u})$ component. Note that the scale in panel A is compressed by a factor of 2 compared with panel B.

intense phonon side band as shown in Fig. 2(a). Unlike the emission, the bands in the corresponding excitation spectrum shown in Fig. 2(b) are again quite sharp. As a consequence of the Franck–Condon principle applied to lattice phonon modes, one usually expects similar appearance of bands of the same transition whether observed in emission or excitation.²⁷ This suggests that in the present case two states may be involved, the absorbing state, and a lower-lying emitting state, populated by nonradiative relaxation.

The bands observed in this region, both in emission and in excitation are listed in Table II. At least eight vibronic transitions are seen in emission. Since the highest energy feature at 19 319 cm⁻¹ is quite weak, it is not *a priori* obvious

TABLE II. Observed As₂ vibronic bands in solid neon. The "yellow" spectrum^{*} $e^{3}\Delta_{\mu} \leftrightarrow X^{1}\Sigma_{e}^{+}$.

| Emission ^b | | Excitation ^c | | | | |
|-----------------------|-----------|-------------------------|-----------|----|-----------|--|
| v" | \bar{v} | v' | \bar{v} | v' | \bar{v} | |
| 0 | 19 745 | 0 | 19 881 | 9 | 22 778 | |
| 1 | 19 319 | 1 | 20 208 | 10 | 23 091 | |
| 2 | 18 894 | 2 | 20 535 | 11 | 23 401 | |
| 3 | 18 470 | 3 | 20 859 | 12 | 23 710 | |
| 4 | 18 048 | 4 | 21 183 | 13 | 24 018 | |
| 5 | 17 631 | 5 | 21 506 | 14 | 24 324 | |
| 6 | 17 214 | 6 | 21 826 | 15 | 24 630 | |
| 7 | 16 800 | 7 | 22 144 | 16 | 24 933 | |
| 8 | 16 388 | 8 | 22 462 | 17 | | |

*All values in cm⁻¹. The wave numbers are accurate to ± 2 cm⁻¹.

^b All emission bands are believed to originate from the $v' = 0 e^{3} \Delta_{u}(2_{u})$ level. See the discussion in the text.

^c All vibronic bands in the excitation spectrum originate in $v'' = 0 X^{1}\Sigma_{g}^{+}$. Only vibrational levels of the $e^{3}\Delta_{u}(1_{u})$ component are observed. whether this is the 0–0 transition or whether additional, still weaker and therefore unobserved bands are present at higher energies. The measured difference between the first and eighth observed band is $2931 \pm 2 \text{ cm}^{-1}$. On the other hand, examination of the data for the red transition show that the spacing between v = 0 and v = 7 is 2946 cm⁻¹ while that between the v = 1 and v = 8 is 2932 cm⁻¹. Clearly, the band at 19 319 cm⁻¹ must be assigned to v = 1 with the unobserved origin of the emission being, by extrapolation, located around 19 745 cm⁻¹.

The lowest energy band in the excitation spectrum occurs at 19 880 cm⁻¹, leaving an interval of 135 cm⁻¹ between the origins of absorption and emission. This confirms that two electronic states are involved. Absorption occurs into the higher state which is connected to the ground state by an orbitally allowed electronic transition. The lower component with transition to ground state forbidden by the symmetry selection rules and therefore unobserved in absorption is populated by a nonradiative relaxation and appears in phosphorescence. This view is further supported by the very long emission lifetime, which varies somewhat depending on matrix history and concentration but is usually in the range of 55 \pm 5 ms.

Very useful in establishing the symmetries of electronic states in matrix isolated molecules can be polarization data,²² which were, for instance, instrumental in assigning the transitions of matrix isolated Sb₂.¹⁵ Unfortunately, the As₂ emissions are quite depolarized suggesting that the As₂ molecules freely rotate, or at least change orientation on the time scale of the lifetime of the emitting states.

Ultraviolet excitation of the matrix produces still another emission spectrum located in the blue. Undispersed, the emission exhibits a double exponential decay. By suitable gating one can observe independently either the short-lived

TABLE III. Observed As₂ vibronic bands in solid neon in the blue and near UV regions^{*} $a^{3}\Sigma_{u}^{-} \leftrightarrow X^{1}\Sigma_{g}^{+}$.

| Emission | | | | Excitation | | | |
|----------|-------------------------|--------------|--------|------------|--------------|------------|--|
| v" | $a(0^+_u)^{\mathrm{b}}$ | $(v'=1)^{c}$ | A 'd | v' | $a(0_u^+)^e$ | $a(1_u)^c$ | |
| 0 | 24 612 | 24 948 | 24 510 | 0 | 24 612 | 24 779 | |
| 1 | 24 186 | 24 522 | 24 084 | 1 | 24 948 | 25 117 | |
| 2 | 23 656 | 23 761 | 23 657 | 2 | 25 280 | 25 449 | |
| 3 | 23 338 | 23 672 | 23 231 | 3 | 25 613 | 25 779 | |
| 4 | 22 916 | 23 246 | 22 806 | 4 | 25 945 | 26 113 | |
| 5 | 22 497 | | 22 385 | 5 | 26 280 | 26 445 | |
| 6 | 22 080 | | 21 969 | 6 | 26 607 | 26 770 | |
| 7 | 21 666 | | 21 553 | 7 | 26 934 | 27 098 | |
| 8 | 21 254 | | 21 144 | 8 | 27 261 | 27 423 | |
| 9 | 20 844 | | 20 733 | 9 | 27 585 | 22 748 | |
| 10 | 20 436 | | 20 312 | 10 | 27 910 | | |

All values in cm⁻¹ with ± 2 cm⁻¹ uncertainty.

^bSharp emission bands originating in the vibrationless $v' = 0 a^{3} \Sigma_{u}^{-} (0_{u}^{+})$ level. No emission is observed from the (1_{u}) component.

^c Weak unrelaxed bands originating in the $v' = 1 {}^{3}\Sigma_{u}^{-}(0_{u}^{+})$ level.

^d A progression of broad emission bands assigned tentatively to a lowerlying $A'^{1}\Sigma_{u}^{-}$ state. Positions of the ZPL's are given. For the first band (in parentheses) the ZPL was not observed and is extrapolated.

^eAll transitions in the excitation spectrum originate from the $v'' = 0 X^{1} \Sigma_{g}^{+}$ level.

or the long-lived component. Spectra from such an experiment are shown in Fig. 3. At short times [Fig. 3(a)] a progression of sharp bands is observed; on the other hand, the longlived emission exhibits a different, spectrally shifted progression of bands show in Fig. 3(b). The lifetime associated with the long-lived spectrum is 20 ± 2 ms. The shortlived bands exhibit a lifetime near 20 ns, too short to be measured accurately with our apparatus. A listing of the vibronic bands observed in this region is given in Table III.



FIG. 3. Low resolution emission spectra of As₂ in solid neon in the blue region. The $a \,{}^{3}\Sigma_{u}^{-}(0_{u}^{+})v' = 4$ level at 25 945 cm⁻¹ was excited. (A) Short-lived emission within a 5 μ s interval containing the laser pulse. It is assigned to the $a \,{}^{3}\Sigma_{u}^{-}(0_{u}^{+})v = 0 \rightarrow X \,{}^{1}\Sigma_{g}^{+}$ transition. (B) Spectrum obtained with a wider (500 μ s) gate. The broadbands are due to emission originating from a lower-lying, probably $A' \,{}^{1}\Sigma_{u}^{-}$ state.

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FIG. 4. A section of the As₂ excitation spectrum in solid neon in the region of the $a^{3}\Sigma_{u}^{-}$ state. Note the alternation of intensities of level assigned to the 0_{u}^{+} and 1_{u} components, respectively.

The appearance of the excitation spectrum, a section of which is shown in Fig. 4, is basically independent of whether the sharp bands, or the long-lived broadbands are monitored. It contains a progression of bands with an average spacing of 165 cm^{-1} . The first of them coincides with the highest energy member of the short-lived emission progression and is therefore clearly the 0-0 band. Both of the blue emission band systems have intensity distributions similar to those of the yellow and red emissions and one might, therefore, expect all of the excited electronic states involved to have similar vibrational frequencies in the neighborhood of $320 \,\mathrm{cm}^{-1}$. An important clue is provided by the spectrum in Fig. 4 which shows alternating lower and higher intensities and also suggests slightly different shapes for the stronger bands. Apparently two absorbing states with interweaved vibrational manifolds are involved. (See Sec. III C.) The fact that the weaker bands are, within experimental accuracy $(\pm 1 \text{ cm}^{-1})$, midway between the neighboring stronger bands is thus apparently fortuitous.

Based on these observations it seems that three electronic states are involved in this region. Two of them, with origins at 24 612 and 24 779 cm⁻¹, respectively (see Table III), are connected to the ground state by orbitally allowed transitions and are observed in the excitation spectrum. Excitation of either of the two states results in population of a third, lower-lying state with origin near 24 510 cm⁻¹ which we label A' and which gives rise to the broad emission bands. The transition between this lower state and the $X^{1}\Sigma_{g}^{+}$ ground state is forbidden, which results in the absence of the vibrational levels due to this state from the excitation spectrum and also produces the broad appearance of the emission bands.

B. Identity of the observed electronic states and As₂ spectroscopy in solid neon

The spectroscopic constants deduced from the data in Tables I-III are summarized in Table IV and, where appro-

TABLE IV. Molecular constants of As_2 in solid neon and in the gas phase (cm⁻¹).

| | | | $T_e^{s)}$ | ω, | ω _e x _e | r _e | τ |
|-----|------------------------------|--------------------------------|------------|----------------------|-------------------------------|----------------|---------|
| GP° | $X^{1}\Sigma_{g}^{+}$ | | 0.0 | 429.5 | 1.12 | 2.1026 | |
| Ne | ••• | (c) | 0.0 | 429.1 | 1.05 | | |
| Ne | ••• | (e) | 0.0 | (431.6) ^b | (1.26) | | |
| Ne | ••• | (a) | 0.0 | 429.8 | 1.11 | | |
| Ne | ••• | (A ') | 0.0 | (431.3) ^b | (1.08) | ••• | |
| G₽° | $c^{3}\Sigma_{u}^{+}1u$ | | 14 481.6 | 314.3 | 1.17 | 2.303 | |
| Ne | ••• | | 14 495.6 | 314.6 | 1.07 | | 12 ms |
| Ne | $e^{3}\Delta_{u}(2_{u})$ | | 19 801.2 | ••• | ••• | | 55 ms |
| GP° | $e^{3}\Delta_{\mu}(1_{\mu})$ | | 19 914.7 | 330.0 | 0.90 | | |
| Ne | ••• | | 19 929.2 | 330.5 | 0.86 | | |
| Ne | $A'({}^1\Sigma_u^-?)$ | | 24 559.3 | | | | 30 ms |
| GP° | $a^{3}\Sigma_{\mu}^{-}$ | (0,+) | 24 641.2 | 337.0 | 0.83 | 2.279 | < 20 ns |
| Ne | ••• | (0 ⁺ _u) | 24 659.8 | 336.3 | 0.60 | | • |
| Ne | $a {}^{3}\Sigma_{u}^{-}$ | (1") | 24 826.3 | 336.8 | 0.69 | | |

^a The T_e values are reported to 0.1 cm⁻¹. Actually, in view of the inhomogeneous effects and experimental factors, the accuracy is $\sim \pm 2$ cm⁻¹. Similarly the ω_e and $\omega_e x_e$ values are given to 0.1 and 0.01 cm⁻¹, while the estimated errors are ± 0.5 and ± 0.1 cm⁻¹, respectively.

^b Derivation of the constants from the broadband spectra involves larger uncertainties of $\sim \pm 2 \text{ cm}^{-1}$ for the ω_e values.

^c The gas phase data are taken from Ref. 28.

priate, compared with the gas phase parameters.²⁸ Four independent sets of values are obtained for ω_e^* and $\omega_e x_e^*$, the $X^1\Sigma_g^+$ vibrational constants, one from each of the four observed emission systems. The ω_e^* constants deduced from the two sharp matrix emissions, 429.1 and 429.8 cm⁻¹, respectively, agree remarkably well with the gas phase value of 429.5 cm⁻¹. The constants calculated from the two broadband emissions, although of lower accuracy, also match the gas phase values satisfactorily.

The visible and near ultraviolet spectroscopy is summarized in the diagram in Fig. 5. Combination of two ground state, ⁴S As atoms yields the $X^{1}\Sigma_{g}^{+}$ As₂ ground state as well as Σ states of multiplicities 3, 5, and 7. The red emission observed in the matrix is clearly due to the lower, 1_{u} , component of the $c^{3}\Sigma_{u}^{+}$ state, analogous to the upper state of the Vegard-Kaplan bands of N₂. The 12 \pm 2 ms lifetime of the emission is considerably shorter than the ~ 3s value in N₂,^{29,30} or ~90 ms in P₂, reflecting the increasing spin-orbit coupling in the heavier As₂. In the still heavier Sb₂ the lifetime shortens further to 625 μ s.

The dissociation energies of the $X^{1}\Sigma_{g}^{+}$ and $c^{3}\Sigma_{u}^{+}$ states are, from the gas phase predissociation studies, known to be ~31 900 and 17 500 cm⁻¹, respectively.²⁸ Sponer extrapolation based on the vibrational levels observed in the matrix yields values of 41 000 and 23 000 cm⁻¹. If one assumes that such extrapolation for the other states observed similarly overestimates the dissociation energies by ~30%, one would predict the upper states of the yellow and blue emissions to converge to atomic products with ~11 000 and 18 000 cm⁻¹, respectively, above the ⁴S + ⁴S limit. Combination of ⁴S + ²D atoms (10 914.6, 10 952.5 cm⁻¹) yields



FIG. 5. Potential energy diagram of As₂. The wiggly arrows denote the observed nonradiative relaxation processes. The "forbidden" states observed in emission $e^{3}\Delta_{u}(2_{u})$ and, probably, $A'^{1}\Sigma_{u}^{-}$ are shown by dashed lines, and the unobserved 0_{u}^{-} component of the $c^{3}\Sigma_{u}^{+}$ state is shown as dotted line. The component splittings are exaggerated for clarity.

 ${}^{3}\Sigma_{u}^{+}, {}^{3}\Pi_{u}, {}^{3}\Delta_{u}, {}^{3}\Sigma_{g}^{+}, {}^{3}\Pi_{g}, \text{and } {}^{3}\Delta_{g}$ electronic states, as well as quintet states of the same symmetry. Considering the corresponding triplet states of N₂ which are all known, 31 one finds that only $W^{3}\Delta_{u}$ and $B^{3}\Pi_{g}$ are strongly bound. The $\Delta\Lambda = 0, \pm 1$ selection rule often breaks down in the matrix and, in fact, the visible spectroscopy of P₂ in neon is dominated by the $w^{3}\Delta_{u}^{+} \leftrightarrow X^{1}\Sigma_{g}^{+}$ transition. We propose that the absorbing state with origin at 19 881 cm⁻¹ (see Table II) is the $\Omega = 1$ component of this state, as is the "e" state observed in the gas phase.

More difficult is the assignment of the emitting state, (origin at 19 745 cm⁻¹) located in the neon matrix 136 cm⁻¹ lower in energy. The w state is expected to be a regular ${}^{3}\Delta_{\mu}$ state, and the $\Omega = 2$ and 3 components should ordinarily be higher in energy. However, both direct spin-spin as well as second order spin-orbit interactions will result in differential shifts of the ${}^{3}\Delta_{\mu}$ components, with the $\Omega = 2$ level being red shifted with respect to $\Omega = 1$ and $\Omega = 3$. This effect was, in fact, observed in the corresponding $w^{3}\Delta_{\mu}$ state of the isovalent P_2 molecule, where the ${}^{3}\Delta_2$ is not midway between ${}^{3}\Delta_1$ and ${}^{3}\Delta_{3}$, but is appreciably downshifted. For a sufficiently large effective spin-spin constant λ the state ordering can, in principle be altered with $\Omega = 2$ becoming the lowest level. Such situation was, in fact, recently reported in the ${}^{3}\Delta$ electronic state of CaO.³² It should be noted that the spin-spin interactions in the As₂ molecule are indeed uncommonly large, with the splitting in the $c^{3}\Sigma_{u}^{+}$ and a ${}^{3}\Sigma_{u}^{-}$ (see below) states, arising from the same electronic configuration as the $e^{3}\Delta_{u}$ state, being 172.8 and 166 cm⁻¹, respectively. We believe, therefore that the fine structure state ordering is indeed inverted in As₂, and assign the emission to the $e^{3}\Delta_{2}$ level. The emitting level could, of course, be due to a different electronic state, with ${}^{3}\Pi_{g}$ and ${}^{1}\Delta_{u}$ appearing to be reasonable possibilities. However, based on comparison of these states in N₂ and P₂, one would predict the corresponding As₂ levels to lie much higher in energy. The ${}^{3}\Pi_{g}$ alternative can, furthermore, probably be safely excluded in view of the long, 55 ms lifetime of the emission. The ${}^{3}\Pi_{g} \rightarrow c \, {}^{3}\Sigma_{u}^{+}$ transition, analogous to the "first positive bands" of N₂ is fully allowed, and the ${}^{3}\Pi_{g}$ state would undoubtedly have a much shorter lifetime due to efficient radiative depopulation. We conclude that assignment to a different electronic state is unlikely, and the $e^{3}\Delta_{2}$ interpretation must be preferred.

It is interesting to note in this context the broad appearance of the emission bands which is probably the consequence of the symmetry forbidden nature of the transition involved. The phosphorescence becomes weakly allowed in the matrix with the lattice phonons breaking the symmetry and being thus the "promoting modes." As a result one observes only weak zero-phonon lines and intense phonon side bands. Several examples of such broadening of forbidden transitions were in fact noted in our parallel study of matrix isolated P_2 .³³

The state responsible for the stronger of the two "blue" progressions appearing in the matrix excitation spectrum with origin at 24 612 cm⁻¹ (Fig. 4), and also observed in emission, is probably identical with the $a^3\Sigma_u^-$ state previously observed in the gas phase. The excellent agreement of the vibrational frequencies ($\omega_e = 337.0 \text{ cm}^{-1}$ in the gas phase, 336.3 cm^{-1} in the neon matrix) lends a strong support to this assignment. The gas phase spectrum was interpreted by Perdigon and d'Incan¹⁹ in terms of a 0_u^+ component of the $a^3\Sigma_u^-$ state correlating with the ²P + ⁴S atomic limit. The second, weaker progression with origin at 24 779 cm⁻¹, 166 cm⁻¹ higher in energy, and exhibiting almost identical vibrational constants ($\omega_e = 336.8 \text{ cm}^{-1}$) is undoubtedly the

previously unobserved 1_u component of the same electronic state. The 166 cm⁻¹ spin-spin splitting in the $a^3 \Sigma_u^-$ state is quite reasonable and very similar to the 172.8 cm⁻¹ value observed in the $c^3 \Sigma_u^+$ state belonging to the same molecular orbital configuration, $(2p\pi_u)^3(2p\sigma_g)^2(2p\pi_g)$.

Uncertain is the assignment of the long-lived emitting state with origin near 24 510 cm⁻¹. Possible candidates would seem to be the states analogous to the $W^1\Delta_u$ or $A'^1\Sigma_u^-$ states of P₂, each of which is expected in this spectral region. In particular, while the $^1\Sigma_u^-$ state lies ~4000 cm⁻¹ above the $^3\Sigma_u^-$ level in N₂, the corresponding states are nearly isoenergetic in P₂. Extrapolation of this trend would predict the $A'^1\Sigma_u^-$ state to be slightly lower in energy in As₂. The $^3\Pi_g$ state can again probably be safely excluded from consideration in view of the possibility of efficient radiative depopulation into the $c^3\Sigma_u^+$ state.

The molecular constants of all the electronic states observed in this work are compiled in Table IV and compared, where available, with the corresponding gas phase values. It is well documented that neon provides a very convenient, nonperturbing medium for spectroscopic studies even of highly reactive intermediates. This was shown quite dramatically by recent studies of molecular ions³⁴ and is also clear from extensive compilation by Jacox of the spectra of matrix isolated diatomics.³⁵ Even so, the lack of medium effects in the case of As, is quite remarkable. For all the four electronic states for which gas phase data are available, the matrix shifts of the ω_e values are less than 0.2%. The electronic shifts of the three excited states at 14 481.6, 19 914.7, and 24 641.2 cm⁻¹ (see Table IV) are 14, 14.5, and 18.6 cm^{-1} , respectively, in each case a blue shift of less than 0.1%.

C. Vibrational and electronic relaxation processes

As we have shown in the preceding section, at least three different excited electronic states of As_2 are found in solid neon not only to emit with appreciable quantum yields, but to have long lifetimes in the millisecond range. In early studies of polyatomic molecules it was noted by Kasha and other investigators that usually only the lowest triplet state, or, in general, the lowest excited state of a given multiplicity is observed in emission. Because of the high densities of states at high energies of excitation, other electronic states usually find efficient nonradiative relaxation pathways. Since the solid matrix provides an effectively continuous density of states, some parallels exist between the relaxation behavior of free polyatomic molecules and small molecules in the matrix. The matrix analog of "Kasha's rule" is, however, often found to be violated.²⁷ Nonetheless, the existence of three independent, extremely long-lived excited electronic states, as seen in As_2 , is quite uncommon.

The lack of efficient radiative relaxation between the excited states must be due to a combination of spin and symmetry selection rules. The relatively inefficient nonradiative relaxation is probably a consequence of the similar, nested appearance of the respective potential curves, which can be seen in the diagram in Fig. 5.

While relatively slow and inefficient, relaxation processes between the individual excited states involved do occur. Thus, excitation in the region of the $e^{3}\Delta_{u}(1_{u})$ state produces, in addition to the "yellow" $e^{3}\Delta_{u}(2_{u})$ emission, also the "red" $c^{3}\Sigma_{u}^{+}(1_{u})$ phosphorescence with a relative quantum yield of ~10%-20%. A part of the excitation spectrum obtained by monitoring the red emission at 12 477 cm⁻¹ and scanning the laser is shown in Fig. 6. In this scan one can identify both the high vibrational levels of the $c^{3}\Sigma_{u}^{+}(1_{u})$ state, as well as the lowest v' = 0-4 levels of the $e^{3}\Delta_{u}(1_{u})$ state. Unlike for direct excitation, when the emission shows no observable rise time and a 12 ms exponential decay, upon excitation of the $e^{3}\Delta_{u}(1_{u})$ state levels the phosphorescence exhibits a clear rise time and a much longer decay time. It is well fitted by the usual expression

$$I = K \left(e^{-\frac{t}{\tau_1}} - e^{-\frac{t}{\tau_2}} \right)$$

when the measured lifetimes of the yellow and red emissions are used for τ_1 and τ_2 , respectively. Clearly, the $c \, {}^{3}\Sigma_{u}^{+}(1_{u})$ state is populated indirectly, via the v = 0 level of the higherlying $e \, {}^{3}\Delta_{u}(2_{u})$ state. Whether this relaxation is entirely nonradiative, or whether some of the energy is lost by emission is



FIG. 6. Excitation spectrum of the $c^{3}\Sigma_{u}^{+} \leftrightarrow X^{1}\Sigma_{g}^{+}$ emission in the region of the $e^{3}\Delta_{u}$ state origin, obtained by monitoring the 0-4 band at 12 744 cm⁻¹. Note the presence of both the lowest $e^{3}\Delta_{u}(1_{u})$ levels, as well as the high $c^{3}\Sigma_{u}^{+}(1_{u})$ levels.



not clear from our data. Such emission would be located in the infrared, far beyond the cutoff of our photomultiplier.

When the $a^{3}\Sigma_{u}^{-}$ state in the near UV is excited, in addition to the "short-lived" and "long-lived" components of the blue emission, both the yellow and red systems are also present. The approximate relative integrated intensities of the four band systems are ~ 1:25:100:25. Some insights into the processes can again be gained by examining the time resolved signals. If the relaxation should proceed via the vibrationless level of the long-lived A' state, both a very long rise time and decay time would be expected for the yellow $e^{3}\Delta_{u}(2_{u})$ emission. Actually, the experimental decay profile is identical to that observed when the low $e^{3}\Delta_{u}(1_{u})$ levels are excited directly; it shows no rise time $(> 1 \, \mu s)$ and a ~ 55 ms decay time. Clearly, the population reaching the $e^{3}\Delta_{u}$ state is bypassing the long-lived A' state.

Further understanding of the processes involved can be gained from Fig. 7 which compares the excitation spectrum of the A' state emission with that of the relaxed $e^{3}\Delta_{u}(2_{u})$ state phosphorescence monitored at 17 631 cm⁻¹. The former in Fig. 7(a) contains the bands at 24 612 and 24 779 cm⁻¹ previously assigned to the 0–0 bands of two components of the $a^{3}\Sigma_{u}^{-}$ state (see Table III), as well as the corresponding v' = 1 levels. In the latter [Fig. 7(b)] one can identify the v' = 1 level of the $a^{3}\Sigma_{u}^{-}(0_{u}^{+})$ state at 24 948 cm⁻¹, but both the v = 0 bands are absent. Instead, a progression of new bands appears with the highest energy one being at 24 933 cm⁻¹. These are easily identified as high vibrational levels of the $e^{3}\Delta_{u}(1_{u})$ state. Apparently, part of the population reaching the 24 948 cm⁻¹ [$v' = 1, a^{3}\Sigma_{u}^{-}(0_{u}^{+})$] level relaxes into the nearly resonant v' = 16 level of the $e^{3}\Delta_{u}(1_{u})$

(A)

(B**)**

251

250

249

24.8

 $\bar{\nu}$ [10³ cm⁻¹]

24.7

a³Σ₀⁻ (0⁺₀)

0 (1₀)

state, only 15 cm⁻¹ lower in energy. Subsequently, fast vibrational relaxation populates the vibrationless level of that state. On the other hand, that part of the population which reaches the v = 0 $a^{3}\Sigma_{u}^{-}(0_{u}^{+})$ level at 24 612 cm⁻¹ can no longer cross into the "e" state, since the nearest $e^{3}\Delta_{u}(1_{u})$ level (v = 17) is now at 24 630 cm⁻¹, 18 cm⁻¹ higher in energy. A small fraction of this population emits directly from the v = 0 $a^{3}\Sigma_{u}^{-}(0_{u}^{+})$ level into the ground state. Most of it, however, (~96%) further relaxes into the v = 0 level of the A' state and gives rise to the long-lived, broadband, blue phosphorescence.

Direct excitation of the $e^{3}\Delta_{u}(1_{u})$ state produces $e^{3}\Delta_{u}(2_{u})$ and $c^{3}\Sigma_{u}^{+}$ state emissions in an approximate ratio of 8:1. When the $a^{3}\Sigma_{u}^{-}$ state is excited a ratio of 4:1 is observed, suggesting that some population reaches the $c^{3}\Sigma_{u}^{+}$ state directly, bypassing the $e^{3}\Delta_{u}(2_{u})$ state. The time resolved emission profile is also indicative of two parallel processes and suggests a prompt component and a delayed component with a long rise time. Whether the relaxation processes are entirely nonradiative or whether part of the energy is disposed of in a radiative step cannot be established from our data.

The observation that the relaxation process is controlled by branching occurring in the v = 1 level of the $a {}^{3}\Sigma_{u}^{-}(0_{u}^{+})$ state raises the question of vibrational relaxation rates and suggests that they might be relatively slow. This is confirmed by the fact that several rather weak bands due to the vibrationally unrelaxed $a {}^{3}\Sigma_{u}^{-}(0_{u}^{+})v' = 1$ emission are clearly observable. Figure 8 shows a small section of the excitation spectrum of the v' = 1 fluorescence. It shows a progression in the $\sim 335 \text{ cm}^{-1} a {}^{3}\Sigma_{u}^{-}(0_{u}^{+})$ state frequency. Conspi-



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24.6

24.5

24.4

15 e ³∆u

14



FIG. 8. A short section of the excitation spectrum of the vibrationally unrelaxed $v' = 1 a^{3} \Sigma_{u}^{-} (0_{u}^{+})$ emission obtained by monitoring the 1'-2" band at 23 761 cm⁻¹. Note the absence of levels due to the (1_{u}) component.

cuously absent are levels of the weaker (1_u) component. This observation on one hand confirms that the vibrational frequency is indeed ~335 cm⁻¹ rather than 167 cm⁻¹, and that overlapping vibrational manifolds of two electronic states are involved as discussed earlier in Sec. III A. On the other hand, it provides additional insight into the relaxation processes. Obviously, vibrational relaxation proceeds predominantly intrastate, within each of the $a^{3}\Sigma_{u}^{-}$ state components. The interstate $1_{u} \rightarrow 0_{u}^{+}$ decay apparently occurs at a slower rate after vibrational relaxation, from the v' = 0 level.

IV. SUMMARY

Evaporation of gallium arsenide provides a convenient, clean source of As_2 molecules. Studies of neon matrices containing As_2 yield spectroscopic information about at least six excited electronic states. Perturbations of the As_2 spectra by the solid medium are found to be remarkably small. The photophysics of this molecule in the condensed phase is unusual in that at least three excited electronic states are found to phosphoresce with very long, millisecond range lifetimes. The various radiative and radiationless processes deactivating the individual states are investigated. The spectroscopy of the As_2 molecule is discussed and summarized.

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