

The FTIR Absorption Spectrum of the Fundamental Band of the AsO Radical

FUMIYUKI ITO,* TAISUKE NAKANAGA,* HARUTOSHI TAKEO,†
KAY ESSIG,‡ AND HAROLD JONES‡

*National Institute of Materials and Chemical Research and †National Institute for Advanced Interdisciplinary Research, Tsukuba Ibaraki, Japan; and ‡Abteilung Chemische Physik, Universität Ulm, D-89069 Ulm, Germany

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An FTIR absorption spectrum of the fundamental band of the AsO radical in its $X^2\Pi_r$ state was measured in the 900–1100 cm^{-1} region with an apodized resolution of 0.006 cm^{-1} . About 1000 transitions with $v'' \leq 3$, $J'' \leq 84.5$ were assigned, based on our previous work [K. Essig *et al.*, *J. Mol. Spectrosc.* **170**, 152–157 (1995)], but some discrepancies were found in the assignments of the $^2\Pi_{3/2}$ – $^2\Pi_{3/2}$ transitions. The transitions were fitted to a $^2\Pi$ Hamiltonian with Hund's case (a) coupling to redetermine the molecular constants in the electronic ground state, including centrifugal distortion of the spin–orbit coupling constants. The r -dependence of the spin–orbit coupling constant $A(r)$ was also determined experimentally. © 1995 Academic Press, Inc.

INTRODUCTION

Among the diatomic oxide molecules of the group Vb elements, AsO has not been observed with a high-resolution spectroscopic technique, in contrast to the NO (1) and PO (2, 3) molecules. The available spectroscopic information for the $X^2\Pi_r$ state of AsO is based on the results of the analysis made by Anderson and Callomon (4). Recently we reported the infrared diode laser spectroscopy of AsO and determined the molecular constants in its electronic ground state (5). In the case of diatomic metal hydrides we have carried out FTIR measurements and combined them with the result of diode laser spectroscopy in order to obtain improved molecular constants as well as the Herman–Wallis factors for these molecules (6, 7). In the present study, as a part of our cooperative study, an FTIR spectrum of the fundamental band of AsO was measured, and an extensive analysis was carried out to redetermine the molecular constants, including higher-order terms in the spin–orbit coupling.

EXPERIMENTAL DETAILS

The method used to produce AsO molecules was essentially the same as that described in (5). A small portion of As_2O_3 powder was placed in an Al_2O_3 tube ($l = 60$ cm), which was heated to about 400°C using Ni–Cr wire. Ar gas was flowed slowly through the cell to maintain the pressure at about 4 Torr. The As_4O_6 vapor (8) was decomposed with a high-frequency AC discharge ($f = 12$ kHz, $I = 300$ mA peak-to-peak) to produce AsO molecules. At first we used the metal flanges which connected the alumina tube to glass inlet tubes as electrodes, but in this case metallic arsenic, which was deposited on the surface of the electrodes, disrupted the discharge. So the electrodes were placed outside the cell,

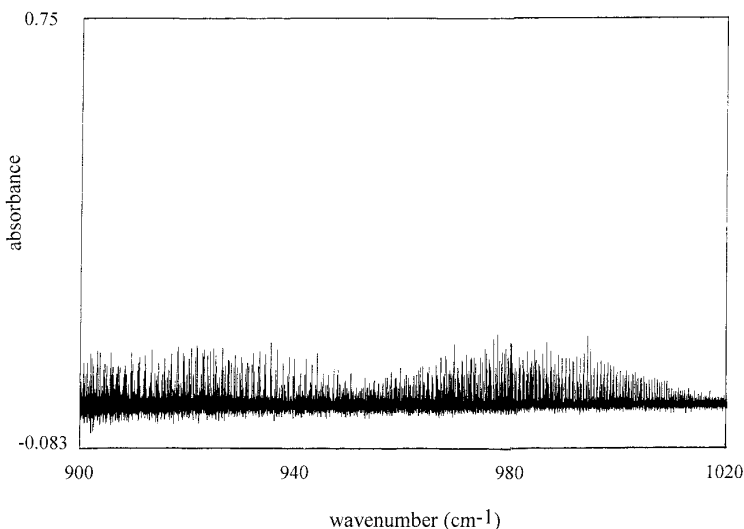


FIG. 1. An overview of the fundamental band of AsO in the 900–1020 cm^{-1} region.

in the inlet tubes, and Ar gas was flowed through them to inhibit the deposition. Modulated infrared light was taken out from the Bomem DA3.36 FTIR spectrometer, passed once through the cell, and detected by a liquid- N_2 -cooled HgCdTe detector. An electrical (<5 kHz) and an optical (<1900 cm^{-1}) low-pass filter were used to eliminate the noise resulting from discharge and infrared emission. The spectrum was recorded in the 900–1100 cm^{-1} region with an apodized resolution of 0.006 cm^{-1} . The use of 71 coadded interferograms gave a noise level on the spectrum of 0.3%. An overview and a small section of the spectrum of AsO are shown in Fig. 1 and Fig. 2, respectively.

ASSIGNMENT AND ANALYSIS

Assignments of all transitions ($v'' = 0, 1, 2, 3$; $\Delta v = +1$) in the $\Omega = \frac{1}{2} \leftarrow \frac{1}{2}$ ladder and of the 1–0 transitions in the $\Omega = \frac{3}{2} \leftarrow \frac{3}{2}$ ladder were carried out straightforwardly using

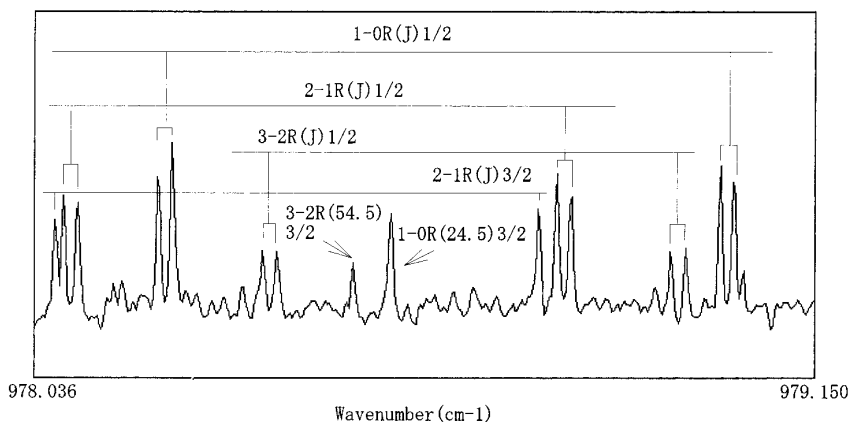


FIG. 2. A small portion of the absorption spectrum of AsO in the *R*-branch region.

molecular constants reported previously (5). However, the assignments of hot bands ($v'' = 1-3$) in the $\Omega = \frac{3}{2} \leftarrow \frac{3}{2}$ ladder could not be made by this method. In the FTIR spectrum, it was found that the transitions in the hot bands previously assigned to the $\Omega = \frac{3}{2} \leftarrow \frac{3}{2}$ subbands were actually one of the Λ -type doubling components in the hot bands of $\Omega = \frac{1}{2} \leftarrow \frac{1}{2}$. On the other hand, several series of unresolved doublets were observed, which are characteristic of $\Omega = \frac{3}{2} \leftarrow \frac{3}{2}$ transitions of a $^2\Pi$ molecule. Therefore reassignments were carried out with the molecular constants of Anderson and Callomon (4). The changes in the assignments for the $\Omega = \frac{3}{2} \leftarrow \frac{3}{2}$ transitions are as follows:

$$2-1: R(20.5) \ 965.3934 \rightarrow 965.2844$$

$$R(18.5) \ 963.7528 \rightarrow 963.6439$$

$$P(10.5) \ 935.9036 \rightarrow 935.8260$$

$$3-2: R(36.5) \ 967.4262 \rightarrow 967.2103$$

With these reassignments, least-squares calculations were carried out iteratively to extend the assignments to higher- J transitions. In total the assignments were made for about 1000 electric-dipole transitions ($\Delta\Omega = 0$). The regions of the assigned $\Omega = \frac{1}{2} \leftarrow \frac{1}{2}$ and $\Omega = \frac{3}{2} \leftarrow \frac{3}{2}$ transitions are shown below:

| v'' | $\Omega =$ | $J''_{\max} (P)$ | | $J''_{\max} (R)$ | |
|-------|------------|------------------|-----------------|------------------|-----------------|
| | | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{1}{2}$ | $\frac{3}{2}$ |
| 0 | | $50\frac{1}{2}$ | $48\frac{1}{2}$ | $82\frac{1}{2}$ | $84\frac{1}{2}$ |
| 1 | | $42\frac{1}{2}$ | $40\frac{1}{2}$ | $79\frac{1}{2}$ | $74\frac{1}{2}$ |
| 2 | | $33\frac{1}{2}$ | $30\frac{1}{3}$ | $71\frac{1}{2}$ | $54\frac{1}{2}$ |
| 3 | | | | $55\frac{1}{2}$ | $54\frac{1}{2}$ |

We also tried to observe the magnetic-dipole transitions ($\Delta v = 0$, $\Omega = \frac{3}{2} \leftarrow \frac{1}{2}$) around 1025 cm^{-1} , the observation of which was reported by Uehara (9), but did not succeed. A center frequency for each transition was determined using least-squares fitting of the observed profile to quadratic functions in the vicinity of the peak center.

The Hamiltonian used in the analysis was essentially the same as that used in (5), and definitions for molecular constants were taken from Burkholder *et al.* (10). But several higher-order constants were added to the Hamiltonian, in order to analyze the extensive data. Matrix elements of the Hamiltonian in Hund's case (a) basis are expressed as

$$\langle {}^2\Pi_{3/2} | H | {}^2\Pi_{3/2} \rangle = T_v + \frac{1}{2}A_v + (B_v + \frac{1}{2}A_{Dv}^{\text{eff}} - D_v - \frac{1}{2}A_H)X - (D_v + \frac{1}{2}A_H)X^2$$

$$\begin{aligned} \langle {}^2\Pi_{1/2} | H | {}^2\Pi_{1/2} \rangle &= T_v - \frac{1}{2}A_v - 2D_v - A_H + (B_v - \frac{1}{2}A_{Dv}^{\text{eff}} - D_v + \frac{1}{2}A_H)(X + 2) \\ &\quad - (D_v - \frac{1}{2}A_H)(X + 2)^2 \pm p_v(J + \frac{1}{2} \pm 1) \end{aligned}$$

$$\langle {}^2\Pi_{1/2} | H | {}^2\Pi_{3/2} \rangle = -(B_v - 2D_v - \frac{1}{4}p_v)X^{1/2} + 2D_vX^{3/2},$$

where

$$X = J(J + 1) - \frac{3}{4}$$

$$T_v = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3$$

$$A_v = A_e - \alpha_A(v + \frac{1}{2}) + \gamma_A(v + \frac{1}{2})^2 - \delta_A(v + \frac{1}{2})^3$$

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2$$

$$D_v = D_e + \beta_e(v + \frac{1}{2})$$

$$A_{Dv}^{\text{eff}} = A_{De}^{\text{eff}} - \alpha_{AD}(v + \frac{1}{2}) + \gamma_{AD}(v + \frac{1}{2})^2$$

$$p_v = p_e - \alpha_p(v + \frac{1}{2}).$$

In the least-squares calculation, a sixth-order centrifugal distortion constant, H_e , was included in the fitting, but it could not be determined with statistical meaning. The Λ -type doubling constant q_e is expected to be small from the value of p_e and the assumption of pure-precession approximation (11):

$$q_e \sim (B/A)p_e = 8.5 \times 10^{-6} \text{ cm}^{-1}.$$

In fact no splitting or broadening due to Λ -type doubling was observed in the $\Omega = \frac{3}{2} \leftarrow \frac{3}{2}$ transitions, so the value of q_e was fixed to zero in the calculation. The equilibrium value of the spin-orbit coupling constant, A_e , which can be determined directly from the observation of magnetic dipole transitions $\Omega = \frac{3}{2} \leftarrow \frac{1}{2}$ (12, 13), was constrained to the value of Anderson and Callomon, 1026.94 cm^{-1} (4), because our attempted observation of any of these transitions was unsuccessful. On the other hand, a v -dependence for A_D , α_{AD} , and γ_{AD} was necessary to reproduce the observed transition frequencies. Only unblended lines in the FTIR spectrum were used in the least-squares calculation and the fitting converged with $\sigma = 0.0010 \text{ cm}^{-1}$. Molecular constants of AsO thus obtained are listed in Table I.

RESULTS AND DISCUSSION

The molecular constants obtained in the present study were slightly different from those in our previous study (5) and the standard deviation of some redetermined parameters is smaller. This is partly due to the number of transitions used in the analysis being increased (diode laser: 144, FTIR: ~ 1000), but the main contribution came from reassignments of the $\Omega = \frac{3}{2} \leftarrow \frac{3}{2}$ transitions. The value of the fourth-order centrifugal distortion constant D_e changed relatively greatly, and the present value ($4.9204 \times 10^{-7} \text{ cm}^{-1}$) agrees well with the estimate from the Kratzer relation (14), $D_e = 4B_e^3/\omega_e^2 = 4.9618 \times 10^{-7} \text{ cm}^{-1}$. The value of r_e was calculated from B_e to be $1.6235271(28) \text{ \AA}$.

Effect of the $\Delta v = 1$, $\Delta \Omega = 1$ Interaction

Since the difference between the values of ω_e and A_e is small ($A_e - \omega_e = 60 \text{ cm}^{-1}$), the energy levels of $^2\Pi_{3/2}(v, J)$ and $^2\Pi_{1/2}(v + 1, J)$ are close to each other. Therefore it was expected that an interaction would exist between these levels ($\Delta v = 1$, $\Delta \Omega = 1$). In this case the following spin-uncoupling operator (15) is relevant in the interaction:

$$H' = -B(r)(J^+S^- + J^-S^+).$$

If this interaction is taken into account as a second-order perturbation, the energy correction is expressed as follows:

$$\delta E = \langle ^2\Pi_{1/2}; v + 1, J | H' | ^2\Pi_{3/2}; v, J \rangle^2 / \Delta E \approx (\omega_e / \Delta E) D_e (v + 1) [J(J + 1) - \frac{3}{4}]$$

$$\Delta E = E(^2\Pi_{3/2}; v, J) - E(^2\Pi_{1/2}; v + 1, J) = 60.32 + 8.662(v + 1).$$

TABLE I
Molecular Constants of AsO in the $X^2\Pi$ State
with One Standard Deviation (in cm^{-1})

| | This work | diode laser [5] | Anderson and Callomon [4] | |
|-----------------------|------------------------------|------------------------------|---------------------------|------------------------|
| | | | $\Omega=1/2$ | $\Omega=3/2$ |
| ω_e | 966.62601(24) | 966.57927(64) | 967.08 | 965.90 |
| $\omega_e x_e$ | 4.91423(11) | 4.89406(31) | 4.85 | 4.909 |
| $\omega_e y_e$ | $-6.5(15) \times 10^{-5}$ | $3.92(37) \times 10^{-4}$ | -1.5×10^{-3} | |
| B_e | 0.4852117(17) | 0.485426(89) | 0.48505 | 0.48529 |
| α_e | $3.31345(12) \times 10^{-3}$ | $3.29735(91) \times 10^{-3}$ | 3.299×10^{-3} | 3.320×10^{-3} |
| γ_e | $-2.132(18) \times 10^{-6}$ | | -4.6×10^{-6} | |
| D_e | $4.9204(54) \times 10^{-7}$ | $6.536(83) \times 10^{-7}$ | 4.9×10^{-7} | |
| β_e | $1.382(27) \times 10^{-9}$ | | 3.0×10^{-9} | |
| A_e | 1026.94 (fixed) | 1026.94 (fixed) | 1026.94 | |
| α_A | 1.16677(49) | 1.2666(13) | 1.18 | |
| A_{De}^{eff} | $2.997(21) \times 10^{-4}$ | $7.05(18) \times 10^{-4}$ | | |
| p_e | $1.7828(99) \times 10^{-2}$ | $1.856(18) \times 10^{-2}$ | 1.76×10^{-2} a) | |
| α_p | $-5.01(23) \times 10^{-5}$ | $-3.06(18) \times 10^{-5}$ | | |
| γ_A | $-6.525(21) \times 10^{-2}$ | $-2.280(62) \times 10^{-2}$ | -5.9×10^{-2} | |
| δ_A | $1.136(29) \times 10^{-3}$ | $2.68(74) \times 10^{-4}$ | 1.9×10^{-3} | |
| A_H | $1.280(52) \times 10^{-8}$ | $3.82(16) \times 10^{-7}$ | | |
| α_{AD} | $1.202(19) \times 10^{-5}$ | $-3.06(18) \times 10^{-5}$ | | |
| γ_{AD} | $-1.850(35) \times 10^{-6}$ | | | |

a) The definition of p in our analysis is the same as that in [10] and the sign of p is opposite to that of [4].

From its J -dependence, the spin-uncoupling interaction perturbs the value of A_D as follows:

$$\delta A_D = 2(\omega_e/\Delta E)D_e(v + 1)$$

From this discussion, it is shown that the value of A_{De}^{eff} is not influenced so much by the perturbation due to spin-uncoupling, because at $v = 0$ δA_D is calculated to be 1.38×10^{-5} , which is one order smaller than the value of A_{De}^{eff} .

r-Dependence of Spin–Orbit Coupling Constant

A spin–orbit Hamiltonian H_{SO} in an electronic state is usually expressed as

$$H_{SO} = \mathbf{A} \mathbf{L} \cdot \mathbf{S},$$

where A is a spin–orbit coupling constant. This constant is obtained by averaging the sum of one-electron spin–orbit coupling operators in one electronic state, and it is dependent on the internuclear distance r . Therefore v -dependence coefficients of $A_v = \langle v | A | v \rangle$, i.e. α_A , γ_A , and δ_A , contain the information about the r -dependence of A

= $A(r)$. James (16) and others (17, 18) have shown the relationship between α_A , γ_A , etc., and r -dependence of $A(r)$,

$$\alpha_A = \frac{\gamma}{2} (3a_1A_1 - 2A_2)$$

$$\gamma_A = \left(\frac{\gamma}{2}\right)^2 \left[\left(-\frac{45}{2}a_1^3 + 39a_1a_2 - 15a_3\right)A_1 + (15a_1^2 - 6a_2)A_2 - 15a_1A_3 + 6A_4 \right]$$

$$A_{De} = \gamma^2 A_1,$$

where

$$\gamma = \frac{2B_e}{\omega_e} = 0.00100393$$

and

$$A_n = \frac{1}{n!} \left[\frac{d^n A(r)}{dr^n} \right]_e r_e^n.$$

Here a_n are the Dunham potential coefficients (19) in the Dunham expansion of the potential function:

$$V(\xi) = \frac{\omega_e^2}{4B_e} \xi^2 \left(1 + \sum_{n=1}^{\infty} a_n \xi^n \right)$$

$$\xi = \frac{r - r_e}{r_e}.$$

The above formulae are valid up to the lowest order of γ in their expansions. Therefore, if we neglect the third-order or higher expansion terms in $A = A(r)$, it is possible to determine A_1 and A_2 from α_A and γ_A obtained experimentally. Dunham potential coefficients were calculated from molecular constants obtained in the present study as follows (19):

$$a_1 = -\frac{\omega_e \alpha_e}{6B_e^2} - 1 = -3.267$$

$$a_2 = \frac{-2\omega_e x_e}{3B_e} + \frac{5}{4} a_1^2 = 6.593$$

$$a_3 = \left[\gamma_e \frac{\omega_e^2}{6B_e^3} - \left\{ 5 + 10a_1 - 3a_2 - 13a_1a_2 + \frac{15}{2} (a_1^2 + a_1^3) \right\} \right] / 5 = -10.78.$$

From these a_n values, A_1 , A_2 were obtained as follows:

$$A_1 = 245.26 \text{ cm}^{-1}, \quad A_2 = -2364.2 \text{ cm}^{-1}$$

From the value of A_1 thus obtained, the value of A_{De} was derived to be $A_{De} = \gamma^2 A_1 = 2.472 \times 10^{-4} \text{ cm}^{-1}$. This value is not so different from the A_{De}^{eff} ($2.997 \times 10^{-4} \text{ cm}^{-1}$) obtained from least-squares fitting, which contains the contribution from the spin-rotation coupling constant γ_{SR} as follows (20):

$$A_{De}^{\text{eff}} = A_{De} - \frac{2B}{A - 2B} \gamma_{\text{SR}}.$$

From the considerations mentioned above, it is shown that:

(a) The v -dependent coefficients, α_A , γ_A , and the centrifugal correction term of the spin-orbit coupling constant, A_{De}^{eff} , were consistently determined, if the expansion of $A(r)$ can be truncated at $(r - r_e)^2$. It has been pointed out that an A_{De}^{eff} obtained experimentally contains a large systematic error when the value of A_e is fixed in the least-squares fit (21). In the present case, this type of error is not so large.

(b) In the electronic ground state of AsO, the r -dependence of the spin-orbit coupling constant $A(r)$ can be expressed as

$$A(r) = 1026.94 + 245.26 \left(\frac{r - r_e}{r_e} \right) - 2364.2 \left(\frac{r - r_e}{r_e} \right)^2,$$

which means that $A(r)$ reaches a maximum in r at $r_{\text{max}} = 1.05187r_e = 1.7077 \text{ \AA}$. A similar r -dependence of $A(r)$, with positive A_1 and negative A_2 values, has been reported in the case of the $X^2\Pi_r$ state of PO molecule (18) and agrees well with the result of a CI calculation (22). We pointed out (5) that the value of α_A/A_e for $\text{PO}(X^2\Pi_r)$ is of the same order of magnitude as that of AsO, but has a different sign. From the present study the difference is due to the fact that the relative magnitudes of A_1 and A_2 in AsO are different from those in PO.

The CI calculation showed that the r -dependence of $A(r)$ in PO ($X^2\Pi_r$) is mainly due to the variation of main electronic configuration, not due to the variation of HOMO in the main configuration. The same situation may hold in the case of AsO, because AsO is isoelectronic with PO. At $r = r_e$, a valence shell of AsO in the ground state is well expressed by one configuration $\sigma^2\pi^4(\pi^*)^1$. Then the spin-orbit coupling constant A^0 in this configuration is expressed as follows (23):

$$A^0 = \langle \pi^* | \hat{a} | \pi^* \rangle; \hat{a} = \sum_K \frac{Z_K}{r_K^3}$$

The main character of the π^* antibonding orbital is $4p\pi$ of the As atom, and the value of A^0 is close to the atomic spin-orbit coupling constant of As ($\xi_{\text{As}} = 1500 \text{ cm}^{-1}$ (24)). In fact, the value of A_e (1026.94 cm^{-1}) is close to the atomic value. With increasing r , the contribution from the 1-electron excited configuration $\sigma^2\pi^3(\pi^*)^2$ increases. From this configuration, we can make the lowest excited $^2\Pi$ state as shown below:

$$\Omega = 1/2: (\pi^+)^2(\pi^-)(\overline{\pi^{*+}})(\overline{\pi^{*-}})$$

$$\Omega = 3/2: (\pi^+)^2(\overline{\pi^-})(\pi^{*+})(\pi^{*-}).$$

The spin-orbit coupling constant A^1 in this excited $^2\Pi$ configuration is expressed as $A^1 = \langle \pi | \hat{a} | \pi \rangle$. The main character of the bonding π orbital is $2p\pi$ of O atom, therefore the value of A^1 is smaller than A^0 , because the atomic spin-orbit coupling constant of oxygen is much smaller than that of As ($\xi_{\text{O}} = 151 \text{ cm}^{-1} \ll \xi_{\text{As}}$). As a result the mixing of the configuration $\sigma^2\pi^3(\pi^*)^2$ in the electronic ground state causes the decrease of spin-orbit coupling constant $A(r)$. The mixing of configurations thus explains the decrease of $A(r)$ in the electronic ground state in $r > r_{\text{max}}$, but the increase of $A(r)$ in $r_e < r < r_{\text{max}}$ cannot be rationalized. Since this increase is relatively small ($A(r) =$

$r_{\max}) - A_e = 6.357 \text{ cm}^{-1}$), it may be due to the minor effect, that is, the variation of π^* orbital in the main configuration.

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