AsH₃ Ultraviolet Photochemistry‡

L. A. Smith-Freeman, W. P. Schroeder, and C. Wittig*

Department of Chemistry, University of Southern California, Los Angeles, California 90089

Received: October 26, 2008; Revised Manuscript Received: December 22, 2008

High-n Rydberg time-of-flight spectroscopy has been used to study the 193.3 nm photolysis of AsH₃. The center-of-mass translational energy distribution for the 1-photon process, AsH₃ + hν → AsH₂ + H, P(Ecm), indicates that AsH₂ internal excitation accounts for ∼64% of the available energy [i.e., hν − D₁(H₂As − H)]. Secondary AsH₂ photodissociation also takes place. Analyses of superimposed structure atop the broad P(Ecm) distribution suggest that AsH₂ is formed with significant α-axis rotation as well as bending excitation. Comparison of the results obtained with AsH₂ versus those of the lighter group-V hydrides (NH₃, PH₃) lends support to the proposed mechanisms. Of the group-V hydrides, AsH₃ lies intermediate between the nonrelativistic and relativistic regimes, requiring high-level electronic structure theory.

I. Introduction

The ultraviolet photolysis of gaseous AsH₃ is germane to the fabrication of semiconductor and electro-optical devices.¹⁻⁴ For example, it has been demonstrated that the 193.3 nm irradiation of AsH₂ can be used to stimulate and manipulate the growth of III–V semiconductor compounds, such as GaAs, InGaAs, and InGaAsP, etc., during metalorganic chemical vapor deposition.²,³ AsH₃ is of fundamental scientific interest, as well. For example, a sensible goal is a quantitative understanding of how molecular properties and photochemical and photophysical mechanisms vary when the lightest group-V hydride, NH₃, is replaced by progressively heavier counterparts (PH₃, AsH₃, SbH₃, BiH₃), i.e., those that span the nonrelativistic and relativistic regimes. High-quality experimental data for the full complement of group-V hydrides would comprise a benchmark against which theoretical models could be tested.

Although there has been a great deal of theoretical and experimental research on NH₃, much less has been done with the heavier group-V hydrides. Experimentalists must contend with toxicity and sample preparation/handling issues, and theoreticians must contend with large numbers of electrons and relativistic effects. The increase in nuclear charge has a pronounced effect on electron velocities, especially for s-orbitals. As speed increases (approaching the speed of light for the heaviest elements), radii decrease and orbital energies are lowered.⁵,⁶ This orbital contraction shields the nuclear charge from the valence electrons, leading to ionization energies, bond energies, and orbital energies that do not follow trends that have been established for lighter atoms.⁵,⁶

Extensive research on the photochemistry and photophysics of NH₃ has yielded high-quality potential energy surfaces (PESs) and a consensus regarding the properties of the lowest excited surfaces and the dynamical processes that transpire on them.⁷⁻¹⁴ This system is a textbook example of predissociation and nonadiabatic dynamics. The ground-state electron configuration is (1a₁)²(2a₁)²(1e)⁴(3a₁)² (C₃ᵥ notation). The promotion of an electron from the lone pair orbital 3a₁ (1a₂ in the D₃h limit) to the 3s a₁ Rydberg orbital accounts for the A₁ → A₁ transition, with its pyramidal-to-planar geometry change. Consequently, the A → X absorption spectrum displays a prominent progression in the ν₂ umbrella mode.

Vibrational levels of the A₁A₂'" state are predissociated to the extent that there is no discernible rotational structure.¹¹ There is a small barrier to dissociation on this surface that arises from the Rydberg-to-valence transformation that accompanies lengthening of the N–H bond.⁷,⁹,¹⁰ The height of this barrier increases with an out-of-plane bend angle (minimizing at planar geometries). For the A₁A₂'" vibrational levels ν₂ = 1 and 2 and dissociation proceeds via tunneling through the barrier. An A/X conical intersection also plays a significant role.⁷⁻¹⁰

Referring to Figure 1, in C₃ᵥ symmetry, NH₃(A) correlates diabatically with NH₃(X₃'B₁), whereas NH₃(X) correlates diabatically with NH₃(A₂''). For nonplanar geometries (θ ≠ 90° in Figure 1), the NH₃ X and A states are each of the same symmetry, and there is an avoided crossing. Consequently, NH₃(A) correlates diabatically with NH₃(A), whereas NH₃(X) correlates with NH₃(X₃'B₁).
TABLE 1: Equilibrium H–M–H Angles for M = N, P, and As and Related Electronic States

<table>
<thead>
<tr>
<th>M</th>
<th>H–M–H Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3 (X1A1)</td>
<td>107</td>
</tr>
<tr>
<td>NH3 (A2A1)**</td>
<td>120</td>
</tr>
<tr>
<td>NH3(X2B2)</td>
<td>103.4</td>
</tr>
<tr>
<td>NH3(A2A1)</td>
<td>144</td>
</tr>
<tr>
<td>PH3 (X1A1)</td>
<td>93.5</td>
</tr>
<tr>
<td>PH3(A2A1)</td>
<td>114</td>
</tr>
<tr>
<td>PH3(X2B2)</td>
<td>91.4</td>
</tr>
<tr>
<td>PH3(A2A1)</td>
<td>123.1</td>
</tr>
<tr>
<td>AsH3(X1A1)</td>
<td>92.1</td>
</tr>
<tr>
<td>AsH3(A2A1)</td>
<td>112</td>
</tr>
<tr>
<td>AsH3(X2B2)</td>
<td>90.4</td>
</tr>
<tr>
<td>AsH3(A2A1)</td>
<td>123</td>
</tr>
</tbody>
</table>

* See text for details and references.

correlates adiabatically with NH3(X). Figure 1 illustrates these aspects of the surfaces.

The barrier and conical intersection influence the dissociation dynamics of NH3(A). Biesner et al. studied this for 0 ≤ v2 ≤ 6 using H atom photofragment translational energy spectroscopy. They found that NH3 is born with significant internal excitation, mainly in the form of a-axis rotation. They concluded that NH3 out-of-plane bending is encouraged by the shape of the potential in the vicinity of the conical intersection, resulting in considerable NH2(X) a-axis rotation. In contrast, near-planar dissociation leads to NH3 with modest a-axis rotation. It is intuitive that umbrella mode vibrational excitation correlates with a-axis rotation. It should be noted that competition between adiabatic and nonadiabatic pathways is energy-dependent, with v2 being a minor channel. The center-of-mass (c.m.) translational energy distribution, P(Ecm), consists of partially resolved structure superimposed on a broad background. Unambiguous assignment is not feasible because the structured features are broad and of modest signal-to-noise ratio (S/N) and there is a significant amount of secondary photoysis.

In consideration of the photodissociation dynamics of NH3 and PH3, it is suggested that the main features arise from AsH2(X) with substantial a-axis rotation as well as bending excitation. Secondary photolysis of AsH2(X) yields AsH. In light of the similarities between the present results and those obtained with PH3, it is interesting that the AsH3 A state has been calculated to be 1E, whereas the PH3 A state is 1A1. The AsH3 system lies intermediate between nonrelativistic and relativistic regimes. An important goal is that this system achieves the same degree of accord between theory and experiment by lighter counterparts.

II. Experimental

The HRTOF arrangement shown in Figure 3 has been discussed previously,26 so only details that are relevant to the present study are given here. A pulsed valve (General Valve, 0.8 mm orifice) expanded mixtures of AsH3 (Matheson Tri-Gas, 99.999%) dilute in a carrier gas (10% in H2, 5% in H2, and 5% in Ar). The molecular beam was collimated 2 cm downstream from the nozzle by a 1-mm-diameter skimmer. At the interaction region, 5 cm downstream from the skimmer, the molecular beam was intersected by the outputs of three pulsed laser systems.
Photolysis radiation was from an ArF excimer laser (Lambda Physik Compex 201). HRTOF spectroscopy probed nascent H atoms by using sequential excitation to high-\(n\) Rydberg levels: 121.6 nm radiation excited H atoms (Lyman-\(\alpha\)), and \(\sim 365\) nm radiation promoted the excited H atoms to a Rydberg state with \(n\) \(\sim 50\). Two Nd:YAG pump lasers (Continuum Powerlite 8010 and 9010) and two dye lasers were used for this “tagging” of the H atoms. The output of one dye laser (Continuum ND6000, LDS 750 dye) was frequency-doubled in a KDP-C crystal, producing 364.8 nm radiation. This was focused into a 10 cm tripling cell, where Lyman-\(\alpha\) radiation was generated by nonresonant frequency-tripling in Kr. Dissociation of AsH\(_3\) by 121.6 nm radiation was negligible due to the low efficiency of the third harmonic generation. The output of the second dye laser (Continuum ND6000, LDS 750 dye) was frequency-doubled, yielding the Rydberg (\(\sim 365\) nm) radiation.

Metastable H atoms that traverse the 43.5 cm flight tube (perpendicular to the interaction region; see Figure 3) are field-ionized and detected with near-unit efficiency by two back-to-back microchannel plates in a chevron configuration. A weak dc field applied to a pair of electrodes surrounding the interaction region eliminates ion background signals and makes space anisotropic for high-\(n\) Rydberg atoms. The output of the second dye laser (Continuum ND6000, LDS 750 dye) was frequency-doubled, yielding the Rydberg (\(\sim 365\) nm) radiation.

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III. Results

An HRTOF spectrum for the photolysis of jet-cooled AsH\(_3\) is presented in Figure 4. Vertical dashed lines indicate the earliest arrival time that can be attributed to primary photolysis using \(D_0(\text{H}_2\text{As} - \text{H}) = 74.9 \pm 0.2\) kcal/mol.\(^{24}\) The signal that precedes the dashed line is evidence of secondary photolysis. Many such spectra were recorded, and no qualitative differences were observed. The one shown in Figure 4 is one of the better ones insofar as S/N is concerned.

Figure 5 shows HRTOF spectra for the photolysis of AsH\(_3\) (10% in H\(_2\)). These traces were obtained using 193 nm energies of 0.5 and 4.2 mJ. The 193 nm radiation is focused using a 100 cm focal length lens, resulting in fluences of \(\sim 5\) and \(\sim 40\) J/cm\(^2\), respectively. Reducing the photolysis fluence lessens the production of fast H atoms that derive from secondary photolysis. However, the broad unstructured one-photon signal was not simplified; it was just of lower intensity. Analogous spectra collected using supersonic expansions of 5% AsH\(_3\) in H\(_2\) and 5% AsH\(_3\) in Ar showed no discernible variations from the spectrum in Figure 4, so they are not presented. The spectrum in Figure 4 was converted to the c.m. translational energy distribution shown in Figure 6a by using the formulas
where \( v_{mb} \) is the molecular beam velocity, \( d \) is the length of the flight tube, and \( r \) is the H-atom arrival time. Referring to eq 2, the measured TOF distribution, \( f(t) \), is converted to the corresponding c.m. translational energy distribution, \( P(E_{c.m.}) \), by using the time-to-energy Jacobian, which is proportional to \( r' \), and the relationship between \( r \) and \( E_{c.m.} \) given in eq 1. Note: \( P(E_{c.m.}) \) applies only to those channels that yield H atoms.

The black dashed line to the right of the red box in Figure 6a indicates the maximum \( E_{c.m.} \) allowed by energy conservation when the H atoms result from primary photolysis. Translational energies in excess of this value derive from secondary photolysis. The inset in Figure 6a shows a fairly abrupt termination of \( P(E_{c.m.}) \) at 51 800 ± 500 cm\(^{-1}\), corresponding to dissociation of AsH\(_2\) with internal energies near \( D_0(\text{HAsH}) = 66.5 \pm 0.02 \text{ kcal/mol}^{24} \) and negligible AsH\(_2\) internal excitation. The value 51 800 ± 500 cm\(^{-1}\) was obtained by deconvoluting the data to account for instrument resolution.

Background subtraction was used to elucidate peaks in the ranges 1000–10 000 cm\(^{-1}\) (Figure 6b) and 14 000–24 000 cm\(^{-1}\) (Figure 6c). The average spacing between peaks in the high-energy region is \( \sim 1000 \text{ cm}^{-1} \), in rough accord with the AsH\(_2\) bend frequency.\(^{30} \) In the low-energy region, the spacing is \( E = 360 \text{ cm}^{-1} \) for the range 1500–5000 cm\(^{-1}\). We interpret this as due to \( a \)-axis rotation in AsH\(_2\)(\( \tilde{X} \)), as discussed in the next section.

### IV. Discussion

The unambiguous identification of the participating pathways and mechanisms in the 193 nm photodissociation of AsH\(_3\), as well as its nascent photofragments, is difficult for several reasons. First, the photon energy exceeds greatly the bond dissociation energies of AsH\(_3\) and AsH\(_2\), thereby enabling highly internally excited fragments to be produced, with a multitude of possible reaction channels. Second, theoretical calculations on AsH\(_3\) and AsH\(_2\) are limited. Third, the presence of significant secondary photolysis adds an unappreciated subtlety to the assignment of the c.m. translational energy distribution. The eye is drawn to the peaks, yet the broad background contains nearly all of the signal and, therefore, the real story. The above points compromise our ability to extract product internal energy distributions.

The goal of this section is a qualitative understanding of the photoinitiated decomposition dynamics of the AsH\(_3\) system, in particular vis-à-vis its NH\(_3\) and PH\(_3\) counterparts. The NH\(_3\) system has received a great deal of attention owing to its experimental accessibility and its relatively straightforward electronic structure. At the same time, it is important to examine heavier counterparts, and AsH\(_3\) is a good candidate, because it lies intermediate between nonrelativistic and relativistic regimes.

#### Primary Photolysis: AsH\(_3\) \( \rightarrow \) AsH\(_2\) + H.

The \( P(E_{c.m.}) \) distribution shown in Figure 6a is broad, with partially resolved structure and a maximum at low \( E_{c.m.} \). Despite the presence of secondary photolysis, an estimate of the “center-of-gravity” of the distribution indicates that AsH\(_2\) internal excitation accounts for ~64% of the available energy [i.e., \( E_{\text{avil}} = h\nu - D_0(\text{HAs} - \text{H}) \)]. This is in agreement with the qualitative result of Koplitz et al.,\(^{28} \) who reported that internal excitation accounts for ~2/3 of the available energy.

Following the absorption of a 193 nm (6.42 eV) photon, the following channels are energetically accessible (also see Figure 2):

\[
\begin{align*}
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}_3(\tilde{X}^2B_2) + H \\
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}_3(\tilde{A}^2A_1) + H \\
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}(X^3\Sigma^-) + H_2 \\
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}(X^3\Sigma^-) + H + H \\
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}(a^1\Delta) + H_2 \\
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}(b^1\Sigma^+) + H_2 \\
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}(A^1\Pi) + H_2 \\
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}(c^1\Pi) + H_2 \\
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}(\tilde{S}) + H_2 + H \\
\text{AsH}_3(\tilde{X}^1A_1) + h\nu_{193} & \rightarrow \text{AsH}(\tilde{D}) + H_2 + H
\end{align*}
\]

Given that AsH\(_2\)(\( \tilde{A} \)) lies 19 909 cm\(^{-1}\) above AsH\(_3\)(\( \tilde{X} \)),\(^{30} \) the maximum \( E_{c.m.} \) that is compatible with reaction 4 is 5600 cm\(^{-1}\).
(see Figure 2). The distribution shown in Figure 6 indicates that reaction 3 dominates, with high AsH₂(X) rotational excitation. This is reasonable in light of the photodissociation dynamics of PH₂.\(^{21-23}\) and NH₃.\(^{12-14,17}\)

Ultrapotent photoexcitation results in a change of equilibrium geometry. The AsH₃(X) electron configuration is \(\cdots (a_1)^2(e)^2(a_1)^2\), and the equilibrium value of the \(\theta_{\text{H-As-H}}\) angle is 92.1\(^\circ\).\(^{27}\) According to the Walsh diagram for this system, promotion of an \(a_1\) lone pair electron to the Rydberg \(a_1\) orbital increases the \(\theta_{\text{H-As-H}}\) equilibrium angle.\(^{37}\) This will excite the \(v_2\) umbrella mode, as in the analogous \(\tilde{A} \rightarrow \tilde{X}\) transitions in NH₃ and PH₂.\(^{9,15}\) It should be noted that the promotion of an \(a_1\) lone pair electron to other excited orbitals in this energy region might also result in umbrella mode excitation.

The photoinitiated dissociation dynamics of NH₃ provides insight. The NH₂ \(\tilde{A} \rightarrow \tilde{X}\) absorption spectrum exhibits a resolved \(v_2\) progression that reflects the pyramid-to-planar geometry change. Experimental studies of the state-selected (i.e., \(v_2\)') photodissociation of NH₃(\(\tilde{A}\)) confirm that NH₂ is formed with significant internal excitation that is primarily in the form of \(a\)-axis rotation.\(^{12,17}\) Not surprisingly, the amount of NH₂ internal excitation increases with photon energy. Moreover, excitation of the NH₂ bend has been observed following dissociation via higher \(v_2\)'.\(^{14,16,17}\) Theory and experiment confirm that dissociation commencing from the \(\tilde{A}\) surface is sensitive to (i) its vibrational state; (ii) geometries and motions sampled during fragmentation; (iii) the topology of the conical intersection region; and (iv) competition between adiabatic and nonadiabatic pathways.\(^{7-14,16,17}\)

Dissociation to ground electronic state products is governed by the \(\tilde{A}/\tilde{X}\) conical intersection. For example, trajectory calculations of Biesner et al. illustrate the intersection’s influence on energy disposal into product degrees of freedom.\(^{15}\) Referring to Figure 1, trajectories are funneled toward the intersection, and nonadiabatic transitions are facilitated by near-planar geometry. Dissociation to NH₂(X) can occur either on the first pass through the intersection region or, if this fails, on a subsequent pass. The intersection region has a large gradient in the angular coordinate, and this promotes NH₂(X) \(a\)-axis rotation. Trajectories that fail to emerge on the NH₂(\(\tilde{A}\)) asymptote in the first pass through the conical intersection region can sample more of the \(\tilde{A}\) surface.\(^{12}\)

Dissociation of NH₃ from higher \(v_2\)' leads to NH₂ with larger amounts of vibrational and electronic excitation.\(^{14,17}\) Competition ensues between adiabatic and nonadiabatic pathways once the threshold for NH₂(\(\tilde{A}\)) has been reached (\(v_2\)' \(\geq 3\)). NH₂(\(\tilde{A}\)) that dissociates via markedly nonplanar configurations, thereby avoiding the conical intersection region, does so on the surface that correlates to NH₂(\(\tilde{A}\)). Loomis et al. used time-resolved Fourier transform infrared emission spectroscopy to investigate 193 nm NH₃ photodissociation.\(^{14}\) They found a bimodal NH₂(\(\tilde{A}\)) rotational distribution that they attributed to near-planar and bent geometries that dissociate. Angular momentum conservation dictates that (for \(J = 0\) parent) the angular momentum of NH₂ is equal and opposite the orbital angular momentum of the fragment pair.\(^{13}\) Dissociation from NH₂(\(\tilde{A}\)) is rapid; i.e., \(~20\) fs. Thus, out-of-plane bending is manifested as \(a\)-axis rotation of the NH₂(\(\tilde{A}\)) product.\(^{14}\)

**AsH₂ Internal Excitations.** Given that a 193 nm photon prepares AsH₃(\(\tilde{A}\)) with significant \(v_2\) (umbrella) vibrational excitation, and in light of the similarities between AsH₃ and PH₃ and between AsH₂ and PH₂, it is reasonable to expect the participating pathways and dissociation dynamics of AsH₃ to resemble those of PH₃. For example, consider the different \(\theta_{\text{H-M-H}}\) equilibrium values that exist between parent and product species. The equilibrium values of \(\theta_{\text{H-P-H}}\) for PH₃(\(\tilde{A}\)) and PH₂(X) are 114° and 91.4°, respectively.\(^{18,38}\) This large difference of 22.6° can lead to significant bending excitation in the PH₂(X) product that accrues via the diabatic surface that correlates PH₃(\(\tilde{A}\)) to PH₂(X).

Note that, in this regard, PH₃ differs (perhaps significantly) from NH₃. The equilibrium values of \(\theta_{\text{H-N-H}}\) for NH₂(\(\tilde{A}\)) and NH₂(X) are 120° and 103.4°, respectively; a change of 16.6°. This is 6° less than the 22.6° change that occurs with PH₃. Without a detailed calculation, however, it is not feasible to infer the degree of vibrational excitation present in the triatom product, given the \(\theta_{\text{H-M-H}}\) equilibrium angles for a parent and its triatom product. Specifically, though the angular change in going from parent to products is large, the degree of vibrational adiabaticity along the reaction coordinate must be assessed.

Because of this vibrational adiabaticity, differences of 22.6° versus 16.6° might result in larger fractional differences in the degree of triatom bending excitation. For example, Lambert et al. observed PH₂ with substantial bending excitation and \(a\)-axis rotation following the ultraviolet photolysis of PH₃.\(^{21}\) In contrast, it is known that NH₂ is formed with a relatively modest amount of bending excitation.\(^{12-14,17}\)

The equilibrium bond angles for AsH₃(\(\tilde{A}\)) and AsH₂(X) are 112° (an estimate based on AsH₃(\(\tilde{A}\)) and PH₃(\(\tilde{A}\))) and 90.4°,\(^{39}\) respectively. These values and their 21.6° difference are close to those of their PH₃ counterparts (114°, 91.4°, 22.6°, respectively). Thus, it is reasonable to expect AsH₂ to be formed with high internal excitation, specifically, \(a\)-axis rotation and bending excitation.

This is consistent with our data. The structure in the \(P(E_{c.m.})\) distribution at low translational energies (Figure 6b) is consistent with AsH₂(X) having significant \(a\)-axis rotation. For example, to rationalize the peaks in Figure 6b, rotational energies for AsH₂(X), which is a near-oblate top (\(\kappa = 0.8034\)),\(^{30}\) were calculated using the formula:

\[
F(J, K_c) = B(J + 1) + (C - B)K_c^2
\]  

where

\[
B = (A + B)/2
\]

Values of rotational constants \(A, B,\) and \(C\) are 7.550, 7.162, and 3.615 \(\text{cm}^{-1}\), respectively,\(^{30}\) and \(F(J, K_c)\) is the rotational energy.

Energy separations between calculated rotational levels matched the lower-energy spacings in Figure 6b. The structure below 5000 \(\text{cm}^{-1}\) is fit with \(J\) values in the range 46–54, as indicated in Figure 7. The large amount of AsH₃(X) internal energy, the complex energy disposal, and the scarcity of spectroscopic data make unique assignment impossible. Other sets of rotational levels also fit the data. However, the peaks cannot be fit using any reasonable choice of vibrational
frequencies. Moreover, the established propensity toward $\alpha$-axis rotation is consistent with low $K_c$ values. For example, including $K_c$ values up to 10 does not alter the fit to the data indicated in Figure 7. The "bottom line" is that these estimates are consistent with AsH$_2(\tilde{X})$ being born with significant $\alpha$-axis rotation.

Figure 6c highlights the structure present at the higher $E_{c.m.}$ values. Separations between peaks (though the data are of low S/N) are comparable to the bend of AsH$_2(\tilde{X})$.$^{30}$ Why does this structure occur at higher translational energy? Again, qualitative guidance is available from NH$_3$. NH$_3(\tilde{A})$ that retains near-$C_3v$ symmetry during dissociation passes through the conical intersection region to form NH$_3(\tilde{X})$ in low rotational states.$^{12}$ Loomis et al. used an impulsive model to rationalize the efficient disposal of energy into NH$_2$ bending excitation for planar dissociation.$^{14}$ AsH$_2(\tilde{A})$ that remains near-planar during dissociation has a high probability of undergoing a nonadiabatic transition. The resulting AsH$_2(\tilde{X})$ will have bending excitation because of the change in the equilibrium bond angle in going from AsH$_2(\tilde{A})$ to AsH$_2(\tilde{X})$ but less $\alpha$-axis rotation than molecules that dissociate having considerable umbrella mode excitation.

Adiabatic and nonadiabatic transitions compete. AsH$_2(\tilde{A})$ arises from AsH$_2(\tilde{A})$ that dissociates mainly from geometries that avoid the conical intersection region. Therefore, AsH$_2(\tilde{A})$ is expected to have $\alpha$-axis rotational excitation. Though the equilibrium angles of AsH$_2(\tilde{A})$ and AsH$_2(\tilde{A})$ (112° and 123°, respectively)$^{26,39}$ differ by a smaller amount than for AsH$_2(\tilde{A})$ and AsH$_2(\tilde{X})$ (112° and 90.4°, respectively), this is not unreasonable to anticipate AsH$_2(\tilde{A})$ bending excitation. AsH$_2(\tilde{A})$ is a near-prolate top ($\kappa = -0.8249$).$^{30}$ Rotational energies were estimated using $F(J, K_a) = \tilde{B}J(J + 1) + (A - \tilde{B})K_a^2$, where $\tilde{B} = (B - C)/2$, and $A$, $B$, and $C$ values are 17.207, 4.920, and 3.740 cm$^{-1}$. Peak separations in Figure 6b could not be fit using these calculated spacings.

**Secondary Photolysis:** AsH$_3$ $\rightarrow$ AsH + H. Our considerations here are restricted to secondary photolysis processes that yield H atom fragments. Channels that yield H$_2$ are not considered. Figures 4–6 indicate that the photodissociation of AsH$_3$ yields AsH$_2$ with significant internal excitation and that this species is photolysed. Energy conservation requires

$$h\nu + E_{AsH_2} - D_0(\text{HAs} - \text{H}) = E_{AsH} + E_{c.m.}$$  \hspace{1cm} (17)$$

where $E_{AsH_2}$ and $E_{AsH}$ are the internal energies of AsH$_2$ and AsH, respectively. For those (infrequent) instances in which $E_{AsH_2} \approx D_0(\text{HAs} - \text{H})$ and $E_{AsH}$ is negligible, $E_{c.m.}$ is approximately equal to $h\nu$. In this case, the photon energy (51 780 cm$^{-1}$) appears as $E_{c.m.}$.

Indeed, the inset in Figure 6a indicates a fairly abrupt termination of $P(E_{c.m.})$ at 51 800 ± 500 cm$^{-1}$. This is also easy to see in the TOF spectrum in Figure 4. Namely, the arrival time for which $E_{c.m.} = h\nu$ is 12.4 ns, which coincides with the sharp onset of signal in the TOF spectrum. Thus, AsH$_2$ is formed with a distribution of internal energies that extends all the way up to $D_0(\text{HAs} - \text{H})$.

Many channels are accessible when AsH$_2$ absorbs a 193 nm photon. Referring to Figure 2, photodissociation of AsH$_2(\tilde{X})$ from even its lowest rovibrational level can, on energetic grounds, access a number of product channels. Because AsH$_2$ contains significant internal excitation, the possibilities are legion.

Though AsH($a') +$ AsH($b'\Sigma^+$) are energetically accessible via secondary photolysis, emission from these species has not been observed following 193 nm excitation.$^{29}$ This can be due to the fact that singlet–triplet emission is weak or that these channels are not accessed. AsH($A'\Pi$) is energetically accessible when AsH$_2(\tilde{X})$ contains more than 1500 cm$^{-1}$ of internal energy prior to its photoexcitation. Nonetheless, AsH($A'\Pi$) has not been detected in emission following 193 nm photolysis of AsH$_2$.

Photodissociation of AsH$_2(\tilde{X})$ that has $E_{AsH_2} \leq D_0(\text{HAs} - \text{H})$ can, on energetic grounds, yield AsH($X$) and AsH($A$) with $E_{c.m.} \leq 51 700$ cm$^{-1}$ and $\leq 21 700$ cm$^{-1}$, respectively. The $E_{c.m.}$ distribution in Figure 6 is broad, peaking at $\sim 6000$ cm$^{-1}$. Vibrational excitation in AsH is expected to be modest on the basis of changes of bond lengths: 1.483 Å in AsH$_2(\tilde{A})$, 3.914 Å in AsH$_2(\tilde{X})$, and 1.580 Å in AsH($\tilde{A}$).$^{32}$ Though PESs are not available, possible pathways can be considered in light of symmetry and spin.$^{30}$ AsH$_2(\tilde{X}'\Sigma^+)$ and AsH$_2(\tilde{B}'\Pi)$ correlate to AsH($\Sigma^+$ + H($\Sigma^+$)), whereas AsH$_2(\tilde{A}'\Delta)$ does not correlate to AsH($\Sigma^+$ + H($\Pi$)). For PH$_2$, it has been noted that $\tilde{A}$ may predissociate via $^2\Sigma^+$ because of spin–orbit interaction.$^{40}$ However, $^2\Pi$ is much higher in energy than $^2\Delta$, so predissociation of $^2\Delta$ via $^2\Pi$ is considered unlikely in the present experiments.

**V. Conclusions**

(1) HRTOF spectroscopy has been used to examine the 193 nm photodissociation of AsH$_3$. Contributions from secondary AsH$_2$ photodissociation are also present. The degree of secondary photodissociation can be minimized, but not eliminated, by using low 193 nm fluences. The experimental method is sensitive only to product channels that give H atoms; that is, an elimination channel such as AsH$_2$ $\rightarrow$ As + H$_2$ cannot be detected using the present arrangement. The main experimental result is a broad $P(E_{c.m.})$ distribution that contains a modest amount of superimposed structure.

(2) The dominant reaction pathway is AsH$_3$ $\rightarrow$ AsH$_2(\tilde{X}) +$ H. Nascent AsH$_2(\tilde{X})$ has considerable rovibrational excitation. The average value of $E_{AsH_2}$ is $\approx 16.300$ cm$^{-1}$, which is $\approx 64\%$ of the available energy: $E_{avail} = h\nu - D_0(\text{HAs} - \text{H})$. The distribution of $E_{AsH_2}$ values extends to values as large as $D_0(\text{HAs} - \text{H})$. For those cases in which $E_{AsH_2} \approx D_0(\text{HAs} - \text{H})$ and $E_{AsH}$ is negligible, AsH$_2$ photodissociation yields $E_{c.m.} \approx h\nu_{193}$. This is manifested as a fairly abrupt termination of $P(E_{c.m.})$ at 51 800 ± 500 cm$^{-1}$ (inset in Figure 6a), which matches $h\nu_{193} = 51 780$ cm$^{-1}$. This confirms that AsH$_2$ is formed with a distribution of internal energies that extends all the way to $D_0(\text{HAs} - \text{H})$.

(3) It is known that AsH$_2(\tilde{A})$ is produced because its fluorescence has been detected,$^{25}$ though its yield could not be determined in the fluorescence measurements. In the present experiments, its yield is found to be modest. This follows from the fact that $E_{c.m.}$ must be $\leq 5600$ cm$^{-1}$ for the AsH$_2(\tilde{A})$ channel (Figure 2), and this energy range accounts for a modest fraction of the observed $P(E_{c.m.})$ distribution. Thus, most of the reactive flux passes from electronically excited AsH$_3$ to ground electronic state products, presumably via a nonadiabatic transition mechanism similar to those of PH$_3$ and NH$_3$.

(4) The 193 nm photolysis of AsH$_3$ has much in common with that of PH$_3$. On the basis of the PH$_3$ experimental data and known PH$_3$, PH$_2$, AsH$_3$, and AsH$_2$ geometrical properties, AsH$_2$ bending excitation is expected. For example, note the differences between equilibrium angles $\theta_{PH_3-M-H}$: 114° $\rightarrow$ 91.4° for PH$_3(\tilde{A})$ $\rightarrow$ PH$_2(\tilde{X})$, and 112° $\rightarrow$ 90.4° for AsH$_3(\tilde{A})$ $\rightarrow$ AsH$_2(\tilde{X})$. The separations between adjacent peaks in the structure present in the high-energy region of the $P(E_{c.m.})$ distribution (Figure 6c) are in qualitative accord with AsH$_2(\tilde{X})$ bending quanta.

(5) Separations between adjacent peaks in the low-energy region of the $P(E_{c.m.})$ distribution are in accord with AsH$_2(\tilde{X})$ rotational levels. This is consistent with a mechanism in which
parent umbrella motion evolves to $a$-axis rotation of the $\text{AsH}_2(\bar{X})$ product, as occurs with the lighter group-V hydrides.

(6) An experimental study of the photodissociation of jet-cooled $\text{AsH}_2$ samples in which there is no contribution from $\text{AsH}_3$ background would resolve a number of issues. For example, this could be achieved by photodissociating $\text{AsH}_3$ in a high-pressure quartz expansion channel and then photodissociating expansion-cooled $\text{AsH}_2$ in spectral regions where $\text{AsH}_3$ does not absorb radiation.

(7) Theory is in good shape for $\text{NH}_3$, but the same is not true for $\text{AsH}_3$. Accurate electronic structure calculations will go a long way toward elucidating mechanisms and provide a detailed quantitative understanding of the photophysics and photochemistry of the full range of group-V hydrides. It is imperative that calculations for the heavier species are done at a high level of theory if experimental results are to be reconciled with confidence.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences. We received many valuable inputs from Aleksey Alekseyev and Jessica Quinn.

References and Notes

(40) Xuan, C. N.; Margani, A. J. *Chem. Phys.* 1994, 100, 7000.