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Radical at 193.3 nm**

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Abstract

Photodissociation of H₂S has been studied at 193.3 nm using H-atom photofragment-translational spectroscopy with mass-spectrometric detection. H + HS(ν) product branching ratios are reported which are not in quantitative agreement with other recent experimental results. Secondary photodissociation of HS radicals has also been observed, showing that both S(³P) and S(¹D) are produced via perpendicular transitions. The HS bond energy was found to be 3.62 ± 0.03 eV.

1. Introduction

The UV photodissociation of H₂S has been the subject of considerable study in recent years, as a detailed understanding of the photodissociation dynamics of triatomic molecules is sought. Several experimental and theoretical studies have started to provide a consistent picture of the excited electronic states involved and the dissociation mechanism, although some discrepancies remain.¹⁻¹¹ It is not clear yet whether dissociation of H₂S at 193.3 nm occurs by predissociation of a bound excited state, or by direct dissociation on a repulsive surface perturbed by a bound state. Concerning the dynamics of the photodissociation, although there is agreement that the HS(v) product vibrational state distribution peaks at v=0, there is not quantitative agreement on the overall vibrational distribution. This paper reports a new study of the HS(v) vibrational distribution using H atom photofragment-translational spectroscopy (PTS) with mass-spectrometric detection. In addition, we have observed the secondary photodissociation of the HS radical at 193.3 nm.

The experimental techniques used to probe the HS product-state distribution from H₂S photodissociation virtually span the range of state-of-the-art methodology. Laser-induced fluorescence (LIF) has been used to state-selectively probe the HS product-state distribution, yielding HS rotational state distributions for HS(v=0 and 1).^{1,6} However, rapid predissociation of vibrationally excited HS

radicals in the $A(2\Sigma^+)$ state¹² prevents determination of the vibrational state distribution by LIF. Photofragment-translational spectroscopy was used in the work of Van Veen et al.² and in the present study as well. Velocity-aligned Doppler spectroscopy (VADS) has been applied by Xu, Koplitz and Wittig in a novel implementation of H-atom translational spectroscopy.³ More recently, very high resolution photofragment recoil spectra have been measured by Welge and co-workers by ionizing the product H atom immediately upon dissociation and measuring the H^+ time-of-flight (TOF) over a specified flight length.⁴ Thus, this system provides an important benchmark for comparison of the reliability of various experimental techniques.

Direct detection and measurement of the translational energy distribution of the photodissociation products of free radicals is typically difficult, due to the difficulties of preparing such reactive species. Even for a diatomic radical, such as HS, there is a paucity of information concerning the photodissociation dynamics. Recently, Welge and co-workers directly observed the predissociation of HS $A(2\Sigma^+) \rightarrow H + S(3P)$ after the dissociation of H_2S at 121.6 nm, along with a process assigned to the three-body dissociation $H_2S \rightarrow H + H + S(1D)$.⁵ The photodissociation of H_2S at 193.3 nm produces HS radicals with up to six vibrational quanta, however, the energetics and kinematics of the HS photofragmentation process allow us to measure the translational energy distributions of H atoms produced with little interference from the H atoms formed in the primary photodissociation of H_2S . Our results show that both $S(3P)$ and $S(1D)$

atoms are produced in the 193.3 nm photodissociation of HS, and provide a new determination of the HS X($^2\Pi$) bond dissociation energy.

2. Experimental

These measurements were performed on a crossed-molecular beams apparatus which was configured for producing intense photolytic D atom beams in a study of the $D + H_2 \rightarrow DH + H$ reaction.¹² A detailed description of the experimental techniques can be found elsewhere,¹³ but the key points will be reviewed here. Figure 1 shows a schematic of the apparatus configured for high-resolution photodissociation studies. A pulsed beam of neat H₂S was produced using a home-built piezoelectric pulsed valve¹⁴ with a 0.5 mm nozzle (1) run at a repetition rate of 100 Hz with 50 torr H₂S stagnation pressure. The pulsed beam was formed in a source chamber (2) maintained at 1×10^{-6} torr by a Varian VHS-10 diffusion pump and liquid nitrogen cryogenic panels. As the beam passed into the photodissociation region, it was collimated by a 6.5 mm tall, 0.75 mm diameter skimmer (3), with a nozzle/skimmer distance of 1.0 cm. The photodissociation region (4) was maintained at 5×10^{-6} torr by a VHS-4 diffusion pump and additional cryogenic panels. The 193.3 nm ArF laser beam (5) produced by a Lambda Physik EMG202MSC excimer laser entered this chamber and crossed the beam 3.0 cm from the nozzle under a mild focus (2mm x 2mm spot size) obtained with two cylindrical lenses (focal lengths of 19 and 24 cm). The

excimer laser was polarized using a 10-plate Brewster-angle stack polarizer, which attenuated $\approx 55\%$ of the laser beam, leaving light with $\approx 95\%$ linear polarization.

Photofragments recoiling from the interaction region passed through a 3.5 x 4.0 mm aperture (6), travelled through the main chamber (7) of the apparatus, then through the three apertures defining the differential pumping regions of the UHV mass spectrometric detector. After passing through the third aperture, the photofragments were ionized in an electron-impact ionizer (8). The resulting ions were extracted (9), mass selected in an RF quadrupole (Extrel) and counted with a Daly ion detector. The dependence of the TOF spectra on mass spectrometer transmission and ionizer settings was carefully studied. To maximize the H atom signal and minimize transmission effects the TOF spectra were measured at a high ion energy (100 eV) using a high-frequency RF inductor circuit (Extrel Model 10, 5 MHz) on the mass spectrometer. The high RF frequency allowed complete mass discrimination even at the high ion energy. Product TOF spectra relative to the dissociation laser pulse were accumulated with a CAMAC-interfaced custom Multichannel Scaler, with 0.15 μ sec temporal resolution. The overall flight path for the neutral photofragments was 39.1 cm, with an uncertainty in the flight path well-represented by a Gaussian with a FWHM of 0.75 cm due to the finite size of the photodissociation and ionization volumes.

H₂S stagnation pressures between 10 and 1000 torr were used in a check of any pressure dependence of the photofragment spectra. The only significant change observed in the spectra over this

pressure range was a slight broadening of the TOF peaks, presumably due to collisions of the nascent H atoms and the formation of H₂S clusters at higher pressures. The results presented here were recorded at 50 torr H₂S stagnation pressure. This pressure was found to produce an intense H₂S beam with negligible broadening of the TOF spectra. All the spectra were recorded under conditions in which much less than 1 dissociation event was recorded per laser shot at the peak of the TOF spectra to avoid missing events due to pulse pileup.

3. Results/Analysis

TOF spectra of the H atom fragments (mass-to-charge ratio $m/e=1$) produced by the photolysis of H₂S at low and high laser fluence are shown in Figure 2(a) and (b), respectively. Spectra were obtained over a range of 12-250 mJ/pulse. To the right of the main peak which corresponds to the production of H + HS($v=0$) in Figure 2(a) the features corresponding to H + HS(v) up to $v=5$ are clearly seen. The power-dependent features at shorter times than the main peak, most visible in Figure 2(b), correspond to H atoms produced in the photodissociation of HS(v) radicals into H + S(³P). Careful examination of the spectra in Figure 2 shows that an additional feature appeared between the H + HS($v=2$) and H + HS($v=3$) peaks as the laser fluence was increased. The kinetic energy of this peak is consistent with the dissociation of HS($v=0$) \rightarrow H + S(¹D), given the known S(³P)/S(¹D) splitting¹⁵ of 9239 cm⁻¹. TOF spectra of HS (m/e

33) and S (m/e 32) were also recorded. The orthogonal detection/molecular beam configuration of this experiment is not ideal for detection of heavy fragments, and the broad velocity distribution in the neat expansion of H_2S prevented the resolution of vibrational states in the m/e 32 and 33 spectra. These spectra did show that the S atom was faster than HS, consistent with the photodissociation of HS by a second 193.3 nm photon.

The yield of the $H_2S \rightarrow H + HS(v)$ and $HS(v) \rightarrow H + S(^3P)$ channels as a function of laser power showed no dependence on the vibrational quanta v . A significantly different yield was observed between the primary and secondary dissociation channels, however. The formation of H_2 via $H_2S \rightarrow H_2 + S$ has been seen at higher photon energies,¹⁶ however, no evidence at $m/e=1$ or 2 was seen for this channel at the dissociation wavelength of 193.3 nm.

In the analysis of photodissociation processes producing H atoms, TOF spectra are often directly inverted to yield center-of-mass kinetic energy distributions.⁴ Although this is typically an excellent approximation, it begins to break down as the velocity of the recoiling H atom decreases. In the present work, the forward convolution method was used to convolute assumed HS product-state distributions with the apparatus function to compare with the experimental results. This approach enables us to assess the contributions of the unresolved $HS(v) \rightarrow H + S$ secondary photodissociation channels as well. Two forward-convolution algorithms were used; a Monte Carlo code and a simpler direct integration. The Monte Carlo code was adapted from a reactive

scattering simulation code used in the analysis of the $D + H_2 \rightarrow DH + H$ reaction.¹³ The Monte Carlo results were corroborated by comparison with the simpler code which is frequently used in our laboratory.¹⁷ The principal parameters used to fit the results are the HS(v) state distributions. HS $^2\Pi_i$ branching ratios and HS rotational distributions were taken from the LIF results⁶ for HS(v=0) and assumed to not vary with vibrational state. In the secondary photodissociation $HS \rightarrow H + S(^3P_J)$, the spin-orbit states of the S atom were assumed to be equally populated.

The summed results of the Monte Carlo simulation of the experiment are shown as the solid lines in the TOF spectra. The vibrational state distribution input to the best fit of the data in Figure 2(a) is indicated in Table 1, along with a tabulation of previous measurements. This vibrational distribution was used to fit all of the other TOF spectra, with the only variable being the laser fluence and polarization. The power dependence of the HS secondary photodissociation relative to the primary process was modelled with a standard kinetic treatment as a sequential first-order process, including saturation of the primary dissociation. Cross-sections for the $H+S(^3P)$ and $H+S(^1D)$ channels of 0.54 and 0.18 relative to the primary photodissociation of H_2S were found to fit the data. The H-SH bond dissociation energy $D_0 = 3.90 \pm 0.03$ eV fit the TOF spectra best, and is in agreement with that found by Welge and co-workers^{4,5}.

For the ground electronic state of the HS radical, $X(^2\Pi_{3/2})$, the bond dissociation energy was found to be $D_0 = 3.62 \pm 0.03$ eV. This

value is 0.09 eV lower than that reported by Schnieder et al.⁵ based on their spectroscopic reassessment of the HS A($2\Sigma^+$) well depth. The HS bond dissociation energy can be used to calculate a heat of formation for the HS radical at 0K, $\Delta_f H_0^0 = 141.49 \pm 2.89$ kJ/mol, at the upper end of the confidence limits on the currently accepted value.¹⁸ Using the independently verified value⁵ for the H-SH bond energy and the literature values for the heats of formation of H and H₂S,¹⁸ the heat of formation $\Delta_f H_0^0$ (HS) = 142.95 ± 0.93 kJ/mol can be calculated. This number is in much better accord with that found using our value for the HS bond dissociation energy as opposed to the higher HS bond energy of ref. 5.

TOF spectra were also measured as a function of polarization angle. Figure 3 shows spectra recorded at $\Theta_{\text{pol}} = 0$ and 90 degrees. The angular distribution of the primary products is well described by $\beta = -0.94$,¹⁹ as previously reported in references 2 and 4, confirming that the primary excitation of H₂S occurs by a perpendicular transition, with subsequent rapid dissociation. As in the previous work,⁴ no evidence was seen for differing anisotropies as a function of HS(ν). The TOF spectra in Figure 3 show that the HS \rightarrow H + S($3P$) channel also occurs by a perpendicular transition with $\beta \approx -1.0$: at $\Theta_{\text{pol}} = 90^\circ$ the HS($\nu=0$) \rightarrow H + S($3P$) signal is larger than the signal from H₂S \rightarrow H + HS($\nu=1$), while at $\Theta_{\text{pol}} = 0^\circ$ the reverse is true. This shows that the HS radical must dissociate rapidly ($\approx 10^{-14}$ sec.) after excitation to a repulsive surface. The much weaker HS \rightarrow H + S($1D$) channel is also fit well assuming a perpendicular transition with rapid dissociation.

4. Discussion

The HS(v) distribution we have measured in the primary photodissociation of H₂S at 193.3 nm is within the uncertainties of the results reported by Van Veen et al.² Qualitatively, there is also agreement between our results and those of Xu, et al.³ and Xie, et al.⁴. In particular, a slight odd/even alternation in intensity as a function of v is observed, consistent with the calculations of Kulander⁹ using the predissociation mechanism proposed by Van Veen et al.² However, our results show significantly less vibrational excitation in the HS product than either of the two most recent experiments.^{3,4} The fits in Figure 4 show the sensitivity of our data to changes in the HS(v) distribution, using the results of references 3 and 4 as shown in Table 1.

Interpretation of the VADS work of Xu et al.³ is complicated by a slow H atom signal at large Doppler shifts. This hinders the extraction of unique HS(v) distributions for large v , and it may be possible to fit the VADS data with a vibrational distribution closer to ours. The H-atom TOF technique of references 4 and 5, however, has no such background problem, and should thus allow unambiguous extraction of the HS(v) distribution. The extraction of the state distribution by direct inversion of the TOF data in reference 4 exaggerates the high HS(v) states to some extent. In addition, mention has been made of possible systematic effects discriminating against the fastest H atoms in laser-based TOF methods.²⁰ Such

effects could reduce the apparent HS($v=0$) intensity, leading to the conclusion of more vibrational excitation.

The mass spectrometric detection scheme used in our experiment may have a small kinetic-energy dependence in the ion transmission function, however, the effect should be negligible as excellent agreement has previously been seen for branching ratios by detecting disparate mass fragments in other experiments using this technique.²¹ It is interesting to note that the theoretical model of Dixon and co-workers predicts less vibrational excitation at shorter wavelengths than the previous experiments,¹¹ in better accord with our results.

The observation of both H + S(3P) and H + S(1D) products from the photodissociation of the HS radical at 193.3 nm can be understood in light of *ab initio* studies of HS potential energy surfaces. The polarization dependence of the signal shows that the transition moment in both cases is perpendicular to the HS bond axis. The photon energy (6.4 eV) at 193.3 nm is too large for excitation to the well-known bound A($^2\Sigma^+$) state. H + S(3P) products may be produced by direct dissociation following excitation from the X($^2\Pi_g$) state to the first $^2\Sigma^-$ repulsive state, as shown in the calculations by Bruna and Hirsch.²² The H + S(1D) products may be formed by direct dissociation on a $^2\Delta$ repulsive state seen in the theoretical calculations.

5. Conclusions

We have carried out precise measurements of the product vibrational-state distribution of HS radicals produced by the photodissociation of H₂S at 193.3 nm. Although the vibrational distribution reported earlier by Van Veen et al.² contains large uncertainties, their ranges are in agreement with the current measurement. The present results are not complicated by the presence of modulated background, however, allowing a more straightforward interpretation. Our results are not consistent with the greater degree of vibrational excitation of the HS radical seen in references 3 and 4. As experimental measurements of product-state distributions are used to test ever more detailed theoretical predictions, it will be essential to have a good cross-calibration between techniques. With the body of information that is being developed on H₂S, this molecule may serve as such a benchmark.

The HS radical was seen to dissociate readily at 193.3 nm, producing both H + S(³P) and H + S(¹D) products. The translational energy released in the secondary photodissociation of HS X(²Π) indicates an HS bond energy of 3.62 ± 0.03 eV. The fast H atoms produced in this secondary photodissociation may be a complicating factor in bulk hot-atom studies which use H₂S as an H atom precursor.

Acknowledgement

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Table 1: Relative Cross Sections for HS(v) Products

HS(v)	This work	Welge ⁴	Wittig ³	Van Veen ²
0	0.728	0.626	0.677	0.895-0.705
1	0.056	0.095	0.046	0.015-0.074
2	0.051	0.083	0.078	0.022-0.058
3	0.037	0.061	0.041	0.022-0.073
4	0.040	0.085	0.065	0.027-0.051
5	0.018	0.040	0.052	0.019-0.039
6	0.001	0.010	0.019	-
>6	-	-	0.022	-

Table 1: HS(v) product state distributions measured in the current experiment compared with previous measurements. The results reported here are sensitive to changes in the state distribution of $\approx 1\%$.

Figure Captions

Figure 1. Schematic cutaway view of the source and detector regions of the apparatus. See text for explanation.

Figure 2. (a) TOF spectrum of H-atom photofragments ($m/e = 1$) measured with a pulse energy of 12 mJ/pulse (laser unpolarized). The solid line is the summed fit to the data, with the various components shown as dashed lines. The marked positions correspond to the $H+HS(v)$ states.

(b) TOF spectrum of H-atom photofragments measured with a pulse energy of 250 mJ/pulse. The marked positions correspond to the $HS(v) \rightarrow H + S(^3P)$ for $v = 0-6$. The peak of the $H + S(^1D)$ channel is also marked.

Figure 3. TOF spectra of H-atom photofragments measured with a polarized laser. (a) laser polarized with E perpendicular to the direction of detection. (b) laser polarized with E parallel to the direction of detection.

Figure 4. Comparison of the experimental data with the vibrational distributions reported in references 3 and 4. The solid line is the best-fit found in this experiment, the short dashed line is the fit using the results of reference 4, and the long dashed line is the fit using the results of reference 3. All results are normalized to the peak of the $H + HS(v=0)$ signal for comparison.

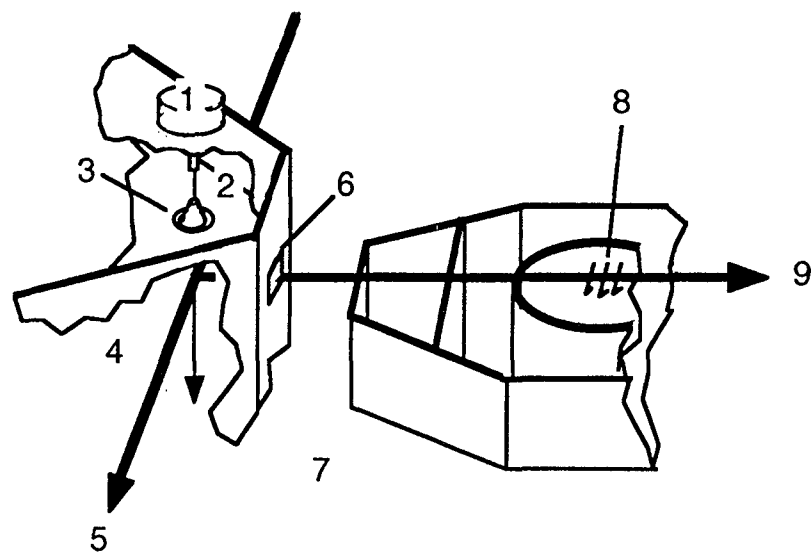


Fig. 1

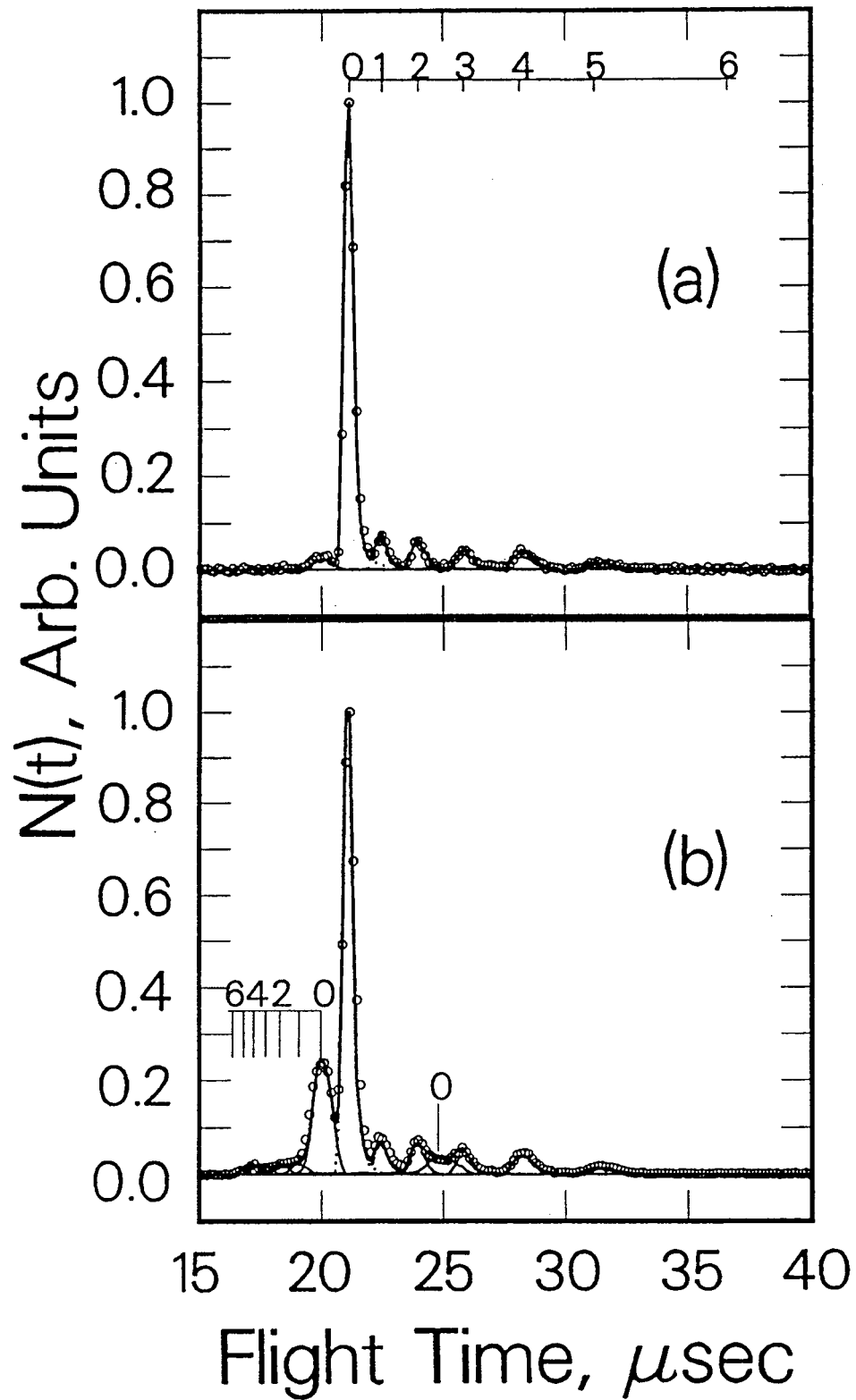


Fig. 2

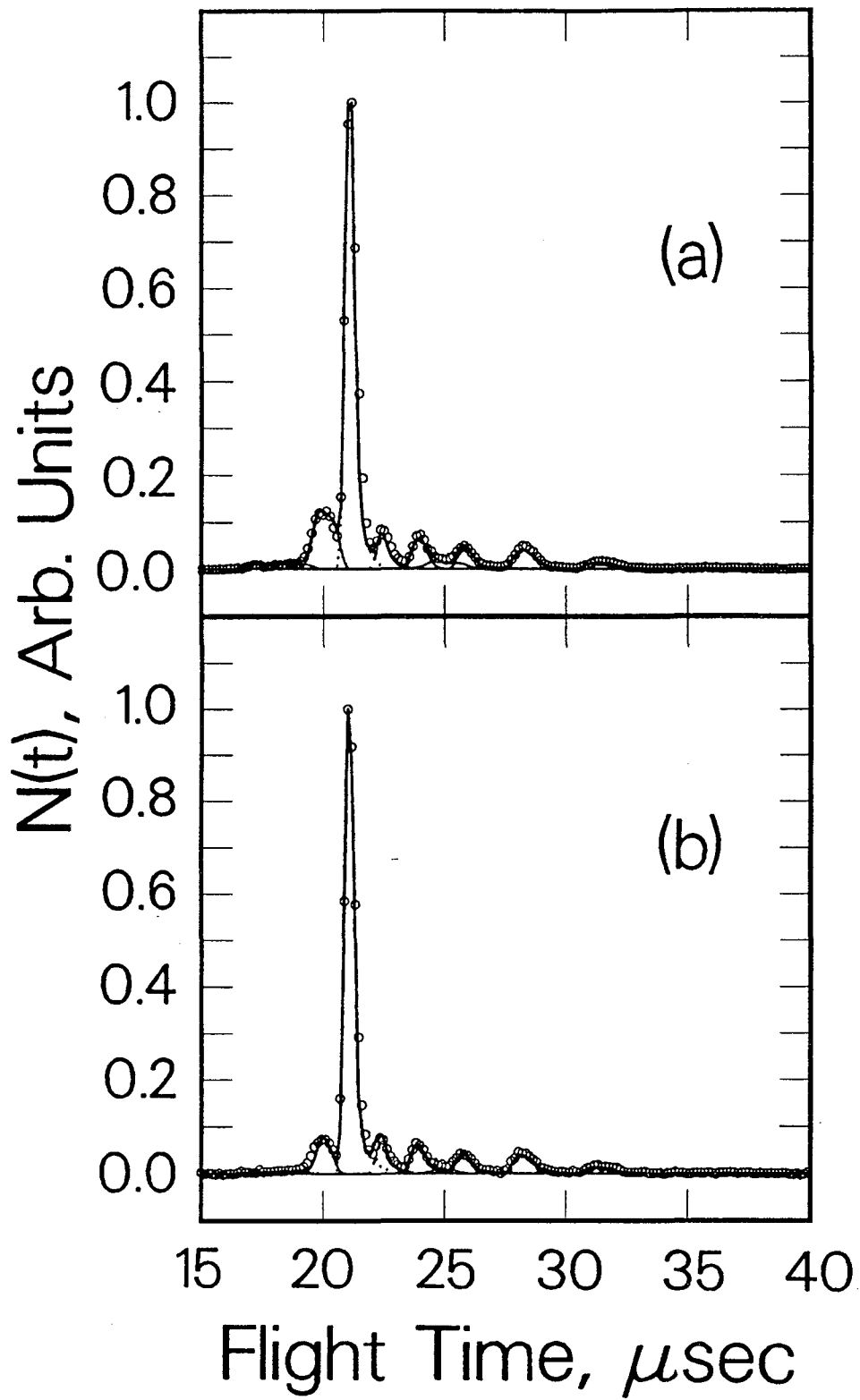


Fig. 3

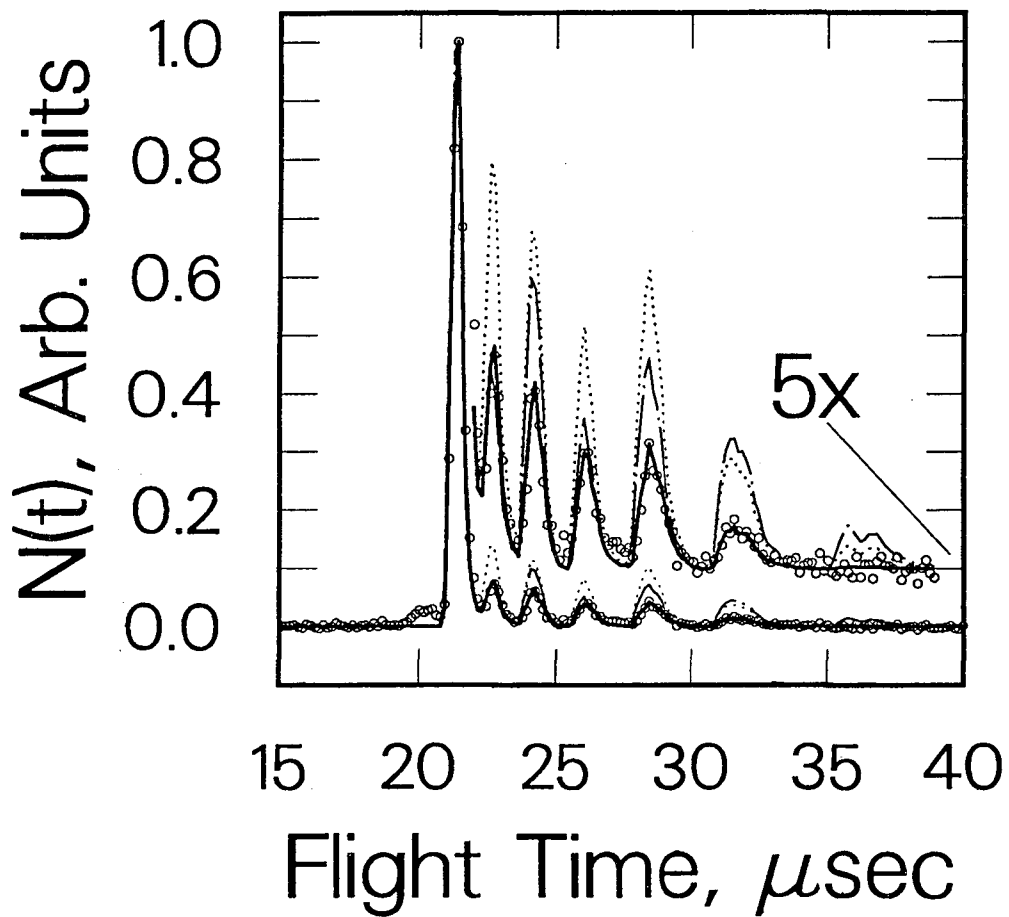


Fig. 4

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