

# LETTERS TO THE EDITOR

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## COMMUNICATIONS

### Coherent phase control of the photoionization of H<sub>2</sub>S

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Coherent phase control was demonstrated for a bound-to-continuum transition of a polyatomic molecule. Three UV photons of frequency  $\omega_1$  and one vacuum ultraviolet (VUV) photon of frequency  $\omega_3=3\omega_1$  simultaneously excited H<sub>2</sub>S above its ionization threshold. The parent ion, H<sub>2</sub>S<sup>+</sup>, and fragment ions, HS<sup>+</sup> and S<sup>+</sup>, produced by absorption of additional photons, were observed. All three ion signals were modulated as the phase difference between the light fields was varied. © 1995 American Institute of Physics.

Controlling the outcome of a chemical reaction has been a long standing goal in reaction dynamics. A number of ways of using coherent light to manipulate the reactants have been proposed over the past decade.<sup>1</sup> One general approach is to exploit the principle of quantum mechanical interference between two competing reaction paths to control the reaction probability.<sup>2</sup> With this method the phase difference between the paths is used to modulate the cross section. A second approach is to use shaped ultrashort light pulses to control the temporal evolution of a wave packet.<sup>3</sup>

Experimental progress in implementing these proposals has been slow. Most demonstrations of coherent control employed weak fields to control transitions in atoms and diatomic molecules. Elliott and co-workers<sup>4</sup> used the competition between one- and three-photon excitation to control the  $6s^1S_0 \rightarrow 6p^1P_1$  transition in Hg, while Gordon and co-workers<sup>5,6</sup> used one and three photons to control rotationally resolved transitions to Rydberg states of HCl and CO. Using a pair of ultrashort light pulses to prepare an excited state wave packet, Scherer *et al.*<sup>7</sup> controlled the  $X \leftarrow B$  transition of I<sub>2</sub>. Baranova *et al.*<sup>8</sup> and Yin *et al.*<sup>9</sup> used one and two photons to control the angular distributions of photoelectrons produced from alkali atoms. Because the continuum states populated in these experiments are orthogonal to each other, control over the total cross section was not possible. Working with intense ( $>10^{13}$  W cm<sup>-2</sup>) fields, Muller *et al.*<sup>10</sup> used 1066 and 533 nm radiation to control the above-threshold ionization of Kr.

Much work remains to be done before active control of chemically interesting reactions becomes a reality. A key step is to demonstrate that it is possible to control transitions in polyatomic molecules. It is also important to show that the total cross section of a bound-to-continuum transition can be controlled with a weak field. It is conceivable that the success achieved so far was due in part to the low state density of atoms and diatomic molecules and in part to the considerable simplification obtained with discrete state-to-state transitions. One might imagine that with thermal mixtures of polyatomic molecules and nonideal light sources the degree

of control possible for bound-to-continuum transitions would be substantially reduced.

We report here the first observation of coherent control of the total cross section of a bound-to-continuum transition in a polyatomic molecule. In this experiment we used the quantum mechanical interference method of Shapiro, Hepburn, and Brumer<sup>11</sup> to control the direct ionization of H<sub>2</sub>S. With this approach, three UV photons of frequency  $\omega_1$  and one VUV photon of frequency  $\omega_3=3\omega_1$  (or wavelength  $\lambda_1=3\lambda_3$ ) simultaneously excite the parent molecule. The transition probability  $P$  is given by the expression

$$P = I_3 S_3 + I_1^3 S_1 + 2[I_3 I_1^3]^{1/2} S_{13} \cos \Delta\phi. \quad (1)$$

Here  $I_1$  is the intensity of the UV beam,  $I_3$  is the intensity of the VUV beam,  $S_1$  and  $S_3$  are the respective absorption coefficients,  $S_{13}$  is a mixed matrix element,<sup>11</sup> and  $\Delta\phi$  is a phase difference,

$$\Delta\phi = \phi_3 - 3\phi_1 + \delta_{13}, \quad (2)$$

where  $\phi_3$  and  $\phi_1$  are the constant terms in the phases of the two light sources, and  $\delta_{13}$  is a molecular term. Equation (1) shows that by experimentally varying  $\Delta\phi$  it is possible to modulate the transition probability.

The apparatus is similar to one described previously.<sup>5,6,12</sup> The UV beam was generated by doubling the frequency of an excimer-pumped dye laser (Lambda Physik Lextra 50 and Scanmate II, DMQ dye,  $\sim 2.0$  mJ/pulse, 10 Hz). Tunable VUV radiation between 117.6 and 118.9 nm was produced from the UV beam by third harmonic generation in  $\sim 5$  Torr of Xe. The phase difference between the two sources was varied by passing the laser beams through a tuning cell containing H<sub>2</sub> gas. Since the refractive index of H<sub>2</sub> differs in the UV and VUV,<sup>12</sup> the relative phases of the two beams is shifted by an amount proportional to the hydrogen pressure. The tuning cell contains a pair of dielectrically coated concave mirrors ( $f=20.3$  cm) which focus both beams into a vacuum chamber. This chamber contains a pulsed valve and a set of Wiley-McLaren<sup>13</sup> electrodes used to extract ions generated by the focused beams. The pressure of pure H<sub>2</sub>S in

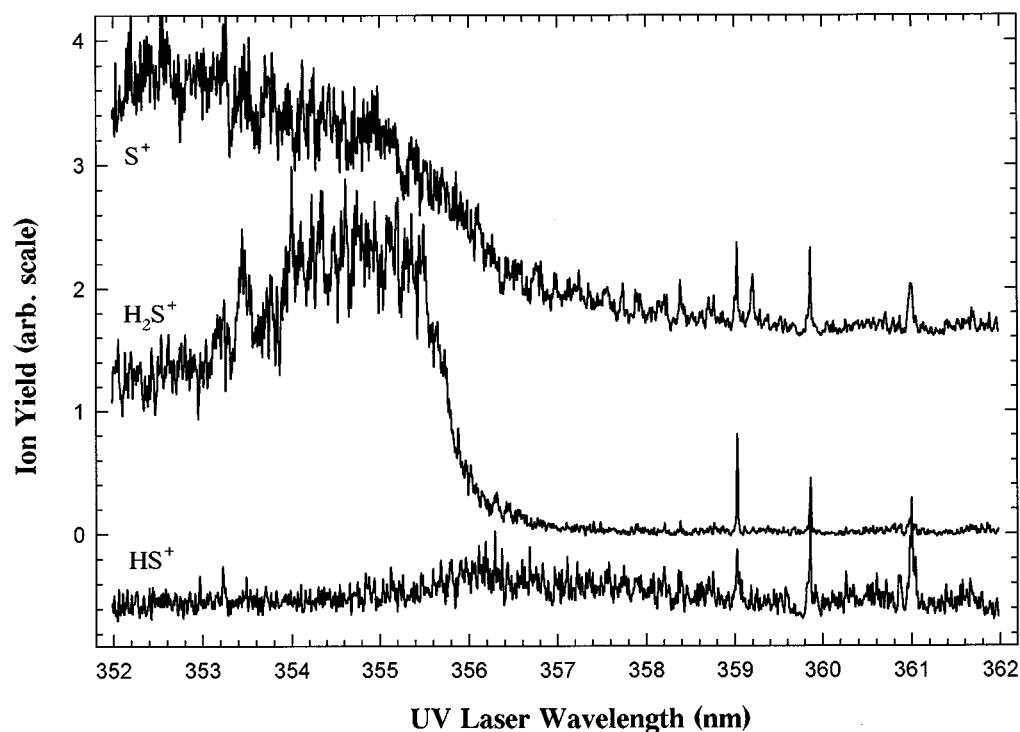


FIG. 1. Intensities of the parent and fragment ions as functions of UV wavelength. The baselines of the  $\text{HS}^+$  and  $\text{S}^+$  signals are shifted for clarity.

the valve was  $\sim 1$  atm. The ions enter a field-free flight tube equipped with einzel lenses, deflection plates, and a micro-channel plate detector. Under our experimental conditions we do not expect any clustering,<sup>14</sup> and no evidence was seen for it.

Figure 1 shows the three-photon spectrum of the parent and fragment ions. The ionization threshold of  $\text{H}_2\text{S}$  near 356 nm is clearly visible. (This experimental threshold is lower than the measured<sup>15</sup> ionization potential of  $84\,432\text{ cm}^{-1}$  because of the Stark shift<sup>16,17</sup> produced by the electric field gradient between the extraction electrodes.) Below the threshold are visible a number of discrete Rydberg transitions. Above the ionization threshold the total ion signal is roughly constant, indicating that a direct ionization mechanism dominates. Intensity dependence measurements between 353.0 and 356.5 nm confirmed that  $\text{H}_2\text{S}^+$  is produced above the threshold shown in Fig. 1 by three photons, while  $\text{HS}^+$  and  $\text{S}^+$  are produced by four or five photons.

Figure 2 shows modulation curves for  $\text{H}_2\text{S}^+$ ,  $\text{HS}^+$ , and  $\text{S}^+$  at  $\lambda_1=355.48$  nm. These signals were generated by adjusting the Xe pressure in the tripling cell so that the contributions to the  $\text{H}_2\text{S}^+$  yield from the UV and VUV sources were approximately equal. The  $\text{H}_2$  pressure  $P_M$  in the tuning cell was then increased from 1 to 7 Torr. The ion peaks have modulation depths of  $\sim 25\%$ , which are comparable to the values obtained for bound-to-bound transitions of HCl with the same optics.<sup>18</sup> The modulations of all three ions are in phase, as is expected, since  $\text{HS}^+$  and  $\text{S}^+$  are produced by photodissociation of  $\text{H}_2\text{S}^+$ . A least-squares fit of the data to the function  $A + B \cos(cP_M + d)$  gives a period of 1.370 Torr for all three curves. This period is proportional to  $n_3 - n_1$  [see Eq. (2) of Ref. 12], where  $n_i$  is the refractive index of

$\text{H}_2$  at  $\lambda_i$ . From the data we obtain a value of  $1 - n_3 = (3.51 \pm 0.06) \times 10^{-4}$  at 118.53 nm, in excellent agreement with the calculated value of  $3.573 \times 10^{-4}$ .<sup>19</sup> Most of the experimental error is due to uncertainty in measurements of the path length. Experiments performed in half nm intervals from 353.0 to 356.0 nm showed similar modulation.

Our results are significant for several reasons. Since the final states of the  $\text{H}_2\text{S}^+$  ion and the ejected electron are governed by one- and three-photon selection rules, there are many angular momentum states reached by three photons that cannot be reached with one photon. For these additional states there is only one path, and control is impossible. Since for each mass we measure the total ion signal summed over all final states, the level of control must be reduced. But since the observed level of control for  $\text{H}_2\text{S}^+$  is comparable to that of the bound-to-bound transitions of HCl,<sup>6</sup> we conclude that the combined probabilities of these additional transitions must be small.

Consider first the rotation of the ion. The change in rotational angular momentum follows a propensity rule  $|N^+ - J''| \leq l''$ ,<sup>20,21</sup> where  $N^+$  is the total angular momentum quantum number of the ion (excluding spin), and  $J''$  and  $l''$  are the total and orbital angular momentum quantum numbers of the initial state. The two-photon<sup>15</sup> zero kinetic energy electron (ZEKE) spectrum of  $\text{H}_2\text{S}$  shows transitions with  $|N^+ - J''|$  greater than those in the one-photon spectrum.<sup>22</sup> On the whole, however, the two spectra are strikingly similar. The tendency for one- and two-photon ZEKE spectra to be very similar has also been reported for NO.<sup>23,24</sup> Although we are unaware of comparable three-photon nonresonant ZEKE spectra, our present results indicate that the one- and three-photon spectra of  $\text{H}_2\text{S}$  should also be quite similar. A general

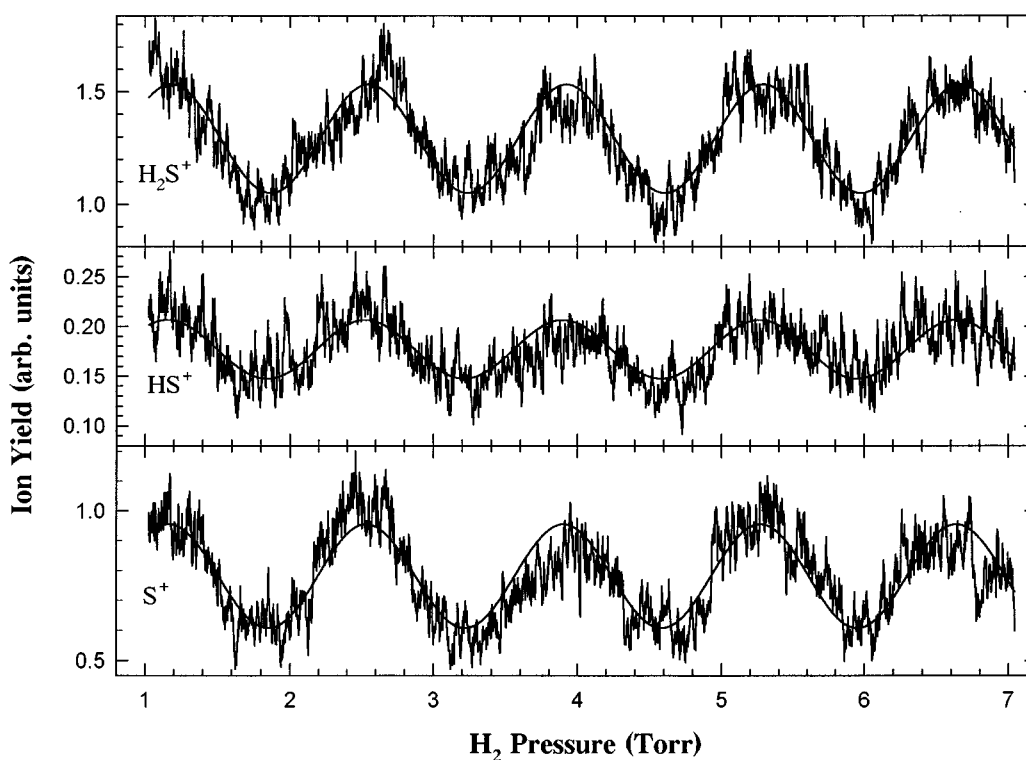


FIG. 2. Parent and fragment ion signals as functions of gas pressure in the phase tuning cell. The smooth curves are least-squares fits of the function  $A + B \cos(cP_M + d)$ .

reason why this should be true is that the rotational line strengths of three-photon allowed, one-photon forbidden transitions are proportional to a third rank tensor multiple moment,<sup>25</sup> and are an order of magnitude smaller than the first rank (both one- and three-photon allowed) line strengths.<sup>26</sup>

Consider next the angular momentum of the electron. The larger change in  $l$  possible for three-photon excitation could substantially reduce the level of control, even though it has only a minor effect on the ZEKE spectrum.<sup>22</sup> For example, in the case of Na ionization, Nakajima *et al.*<sup>27</sup> calculated that at some wavelengths the production of  $f$  waves by three photons dominates and no control is possible, while at other wavelengths  $p$  waves dominate and strong modulation could be achieved. One reason why this may not be a problem here is that scattering of the photoelectron by the non-spherical ion core increases the range of  $l$  for both one and three photons.<sup>28</sup> Another factor is that the electric field gradient between the electrodes promotes  $l$  mixing,<sup>17</sup> thereby diminishing the differences between one- and three-photon excitation. If more than one final value of  $l$  is present, it follows that for H<sub>2</sub>S the molecular phase  $\delta_{13}$  is insensitive to  $l$ .

From our study we also conclude that thermal averaging does not have much of an effect. Rotational cooling in our molecular beam is inefficient, and many states of H<sub>2</sub>S are initially populated. We conclude therefore that for this molecule  $\delta_{13}$  is insensitive to the initial rotational quantum numbers. Our observation of robust control of the ionization of a triatomic molecule by direct excitation to the continuum

leads us to believe that control of bound-to-continuum processes in still larger molecules should be possible.

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<sup>1</sup>W. S. Warren, H. Rabitz, and M. Dahleh, *Science* **259**, 1581 (1993).

<sup>2</sup>P. Brumer and M. Shapiro, *Acc. Chem. Res.* **22**, 407 (1989).

<sup>3</sup>D. J. Tannor and S. A. Rice, *Adv. Chem. Phys.* **70**, 441 (1988).

<sup>4</sup>C. Chen, Y.-Y. Yin, and D. S. Elliott, *Phys. Rev. Lett.* **64**, 507 (1990); C. Chen and D. S. Elliott, *ibid.* **65**, 1737 (1990).

<sup>5</sup>S. M. Park, S. Lu, and R. J. Gordon, *J. Chem. Phys.* **94**, 8622 (1991).

<sup>6</sup>S. Lu, S. M. Park, Y. Xie, and R. J. Gordon, *J. Chem. Phys.* **96**, 6613 (1992).

<sup>7</sup>N. F. Scherer, R. J. Carlson, A. Matro, M. Du, A. J. Ruggiero, V. Romero-Rochin, J. A. Cina, G. R. Fleming, and S. A. Rice, *J. Chem. Phys.* **95**, 1487 (1991).

<sup>8</sup>N. B. Baranova, I. M. Beterov, B. Ya. Zel'dovich, I. I. Ryabtsev, A. N. Chudinov, and A. A. Shul'ginov, *JETP Lett.* **55**, 439 (1992).

<sup>9</sup>Y. Y. Yin, C. Chen, and D. S. Elliott, *Phys. Rev. Lett.* **69**, 2353 (1992).

<sup>10</sup>H. G. Muller, P. H. Bucksbaum, D. W. Schumacher, and A. Zavriyev, *J. Phys. B* **23**, 2761 (1990).

<sup>11</sup>M. Shapiro, J. W. Hepburn, and P. Brumer, *Chem. Phys. Lett.* **149**, 451 (1988).

<sup>12</sup>R. J. Gordon, S. Lu, S. M. Park, K. Trentelman, Y. Xie, L. Zhu, A. Kumar, and W. J. Meath, *J. Chem. Phys.* **98**, 9481 (1993).

<sup>13</sup>W. C. Wiley and I. H. McLaren, *Rev. Sci. Instrum.* **26**, 1150 (1955).

<sup>14</sup>B. R. Weiner, H. B. Levene, J. J. Valentini, and A. P. Baronavski, *J. Chem. Phys.* **90**, 1403 (1989).

<sup>15</sup>I. Fischer, A. Lochschmidt, A. Strobel, G. Niedner-Schatteburg, K. M uller-Dethlefs, and V. E. Bondybey, *J. Chem. Phys.* **98**, 3592 (1993).

<sup>16</sup>W. A. Chupka, *J. Chem. Phys.* **98**, 4520 (1993).

- <sup>17</sup>S. T. Pratt, *J. Chem. Phys.* **98**, 9241 (1993).
- <sup>18</sup>See Fig. 4 of Ref. 6.
- <sup>19</sup>W. J. Meath (private communication).
- <sup>20</sup>R. N. Dixon, G. Duxbury, M. Horani, and J. Rostas, *Mol. Phys.* **22**, 977 (1971).
- <sup>21</sup>M. S. Child and C. Jungen, *J. Chem. Phys.* **93**, 7756 (1990).
- <sup>22</sup>K. Wang, M.-T. Lee, V. McKoy, R. Wiedmann, and M. G. White, *Chem. Phys. Lett.* **219**, 397 (1994).
- <sup>23</sup>R. T. Wiedmann, M. G. White, K. Wang, and V. McKoy, *J. Chem. Phys.* **98**, 7673 (1993).
- <sup>24</sup>A. Strobel, I. Fischer, J. Staecker, G. Niedner-Schatteburg, K. Müller-Dethlefs, and V. Bondybey, *J. Chem. Phys.* **97**, 2322 (1992).
- <sup>25</sup>R. N. Dixon, J. M. Bayley, and M. N. R. Ashfold, *Chem. Phys.* **84**, 21 (1984); M. N. R. Ashfold, *Mol. Phys.* **58**, 1 (1986).
- <sup>26</sup>J. B. Halpern, H. Zacharias, and R. Wallenstein, *J. Mol. Spectrosc.* **79**, 1 (1980). See especially Fig. 3.
- <sup>27</sup>T. Nakajima, P. Lambropoulos, C. Cavalieri, and M. Matera, *Phys. Rev. A* **46**, 7315 (1992).
- <sup>28</sup>M.-T. Lee, K. Wang, V. McKoy, R. G. Tonkyn, R. T. Wiedmann, E. R. Grant, and M. G. White, *J. Chem. Phys.* **96**, 7848 (1992); M.-T. Lee, K. Wang, and V. McKoy, *ibid.* **97**, 3108 (1992); M.-T. Lee, K. Wang, V. McKoy, and L. E. Machado, *ibid.* **97**, 3905 (1992).