PHOTODISSOCIATION CROSS SECTION OF LiI *

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A pulsed tunable UV laser was used to photodissociate LiI. Lithium atoms were detected by three-step resonance ionization spectroscopy (RIS) to obtain absolute dissociation cross sections from 270 to 312 nm. A comparison of the present cross sections at $T = 140°C$ with absorption data at higher temperature ($T = 745°C$) shows that dissociation is a dominant channel following photon absorption. We infer that the repulsive upper state of the corresponding transition crosses the ionic ground-state potential curve.

1. Introduction

In this paper we describe saturated photodissociation of LiI followed by saturated resonance ionization spectroscopy (RIS) detection of Li. RIS is a multistep photoionization process in which high-intensity laser pulses of appropriate wavelength remove single electrons from each atom of a selected type. The general features of the RIS technique, together with its present major applications, have recently been reviewed [1]. In a study on CsI it was shown that in a well-focused UV laser beam all CsI molecules could be dissociated into neutral Cs and I atoms in their ground states. Combined with saturated RIS of Cs, single molecules of CsI can be detected [2]. Whereas, because of a violation of the non-crossing rule, dissociation into ground-state atoms was to be expected for CsI, the situation in LiI is slightly more complicated [3–5]. We show that the dissociation cross section for LiI at the first UV maximum (near 295 nm) is of the same magnitude as the absorption cross section determined by Davidovits and Brodhead [6], which means that dissociation of the molecule is a dominant channel following photon absorption.

2. Experiment

The experimental arrangement used in this work is essentially the same as that described in a paper on RIS of lithium [7]. A sample of LiI crystals, heated to about 470°C and temperature stabilized to ±0.3°C, provided free LiI molecules into a parallel-plate ionization chamber filled with 2.67×10^4 Pa (i.e., 200 Torr) of argon at room temperature. The actual gas temperature between the field plates – 5 cm above the source, where the photodissociation occurred – was measured to be 140°C. After measuring the dissociation cross section, the number density of LiI molecules under these conditions was calculated to be of the order of 10^7 molecules/cm^3.

A 1 μs pulse from a commercial flashlamp-pumped dye laser with intracavity frequency doubling was used to photodissociate LiI vapor along the beam axis. Free Li atoms were detected about 30 μs later by two simultaneously fired dye lasers tuned to the 2S–2P (670.8 nm) and 2P–3D (610.4 nm) transitions in lithium. Ionization out of the 3D level was accomplished by another photon of either of the two red-wavelength lasers within the same pulse. As shown in ref. [7], the photoionization of Li can be saturated in this way which means that a free electron can be produced from each Li atom inside the volume of the two coaxial detector laser beams. The electrons were drifted by an electric field of 80 V/cm to the positive

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field plate. The resulting signal was amplified and processed with a PDP-11 computer-based data-acquisition system (see ref. [8] for more details).

The wavelength of the UV light was measured by using an optical multichannel analyzer equipped with a 0.25 m spectrometer, and the energy per pulse was monitored by a photodiode which was calibrated for each wavelength used against a Scientech surface-absorbing calorimeter.

For an unfocused UV laser beam typically 2 mm in diameter, an energy of 40 μJ/pulse, and a corresponding fluence of about 2×10^{15} photons/cm^2 per pulse, the number of dissociated molecules was a linear function of the number of photons per pulse (upper curve in fig. 1). The relative cross section for photodissociation as a function of wavelength was determined by using the slopes of the various straight lines taken in the wavelength region from 270 nm to 312 nm. This region was covered by two different dyes: coumarin 522 below 290 nm and rhodamine 6G above 290 nm (with a small overlap region around 290 nm).

By focusing the UV beam with a 25 cm focal-length lens down to a diameter of 0.1–0.2 mm (corresponding to a fluence of the order of 10^{17} photons/cm^2 per pulse), saturation of the dissociation process could be achieved (lower curve in fig. 1). Analysis of the saturation curve combined with determination of the actual beam profile within the collection region of the ionization chamber, yielded an absolute value for the photodissociation cross section at 300 nm.

3. Results

Fig. 2 shows the absolute cross section for photodissociation between 270 nm and 312 nm measured at $T = 140°$C. The dashed line is the absorption cross section from Davidovits and Brodhead [6] (at 745°C) with a peak value of $(1.4^{+0.4}_{-0.3}) \times 10^{-17}$ cm^2 at 294 nm. The solid line is a hand-made smooth fit through our data points.

An absolute value for the cross section (at 300 nm) can be obtained from the two curves in fig. 1 without knowing the number density of LiI molecules inside the ionization chamber.

The following analysis was made [2]: n_ℓ = number of dissociated molecules per unit of length, N = number density of LiI molecules, $\phi(\rho) = \phi_0 h(\rho)$ = photon fluence as a function of distance from beam axis (assuming cylindrical symmetry), $h(\rho)$ = experimentally determined beam profile using an 11 μm pinhole, ϕ_0 = fluence at $\rho = 0$, σ = photodissociation cross section,

$$N_\mathrm{p} = \int_0^\infty 2\pi\rho\,\mathrm{d}\rho\,\phi(\rho) = 2\pi\phi_0 \int_0^\infty \rho\,\mathrm{d}\rho\,h(\rho)$$

= number of photons per pulse,

$$n_\ell = N \int_0^\infty 2\pi\rho\,\mathrm{d}\rho\,\{1 - \exp[-\sigma\phi_0 h(\rho)]\},$$

if we assume a uniform density of LiI molecules.

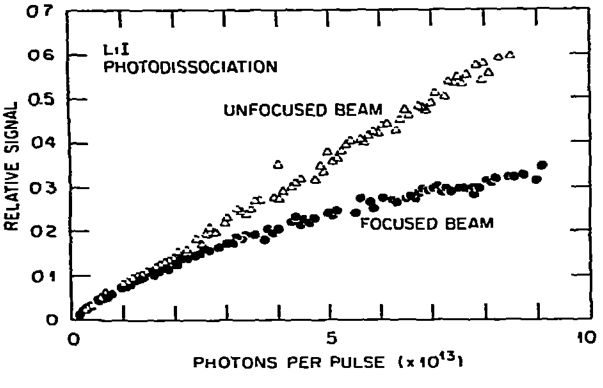

Fig. 1. Relative number of detected Li atoms as a function of the number of photons in a single pulse of the UV laser that dissociates LiI. Data are shown for unfocused and focused beams.

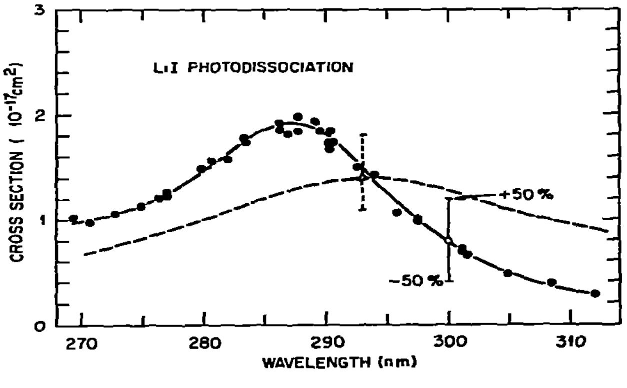

Fig. 2. Cross section for the photodissociation of LiI as a function of wavelength at $T = 140°$C. The broken line is the absorption cross section from Davidovits and Brodhead at $T = 745°$C [6].

Set $x = \sigma\phi_0$ and $n_Q/N = G(x)$, then

$$G(x) = \int_0^\infty 2\pi\rho \, d\rho \, \{1 - \exp[-xh(\rho)]\}$$

for the focused beam; and for $x \ll 1$,

$$G_0(x) = xN_p/\phi_0$$

applied to the unfocused beam. The ratio $R(x) = G(x)/G_0(x)$ was calculated by numerical integration of measured beam profiles, and the cross section was found to fit the experimental ratio of the two curves in fig. 1.

Due to the improved computer-based data acquisition, it was not even necessary actually to measure the linear function $G_0(x)$ (upper curve in fig. 1); its slope could be calculated from the slope of a fifth-order polynomial fit to the saturated curve (lower curve in fig. 1) at low numbers of photons per pulse.

Our analysis yielded an absolute value of 0.8 × 10^{17} cm^2 at 300 nm. Random errors in energy calibration and curve fitting together with known variations of the beam profile along the 1.2 cm collection path, would have allowed us to set error limits of about ±20% to an absolute value, but several repetitions of the calibration on different occasions indicated larger variations of ±50%. Since the LiI molecules are supplied from the hot source to the laser beam in a convection process, we believe that density gradients are a possible cause of this uncertainty.

4. Discussion

Among the alkali halides, LiI has some unique features. According to Berry's curve-crossing theory [3], the first excited electronic state with the same symmetry as the Σ^+ ground state should show an avoided crossing at the first crossing point; therefore, LiI is expected to have a bound-state spectrum. Such a spectrum was not observed in the gas phase, and Berry suggested that the repulsive part of the upper curve is shifted to greater internuclear distances and, therefore, not accessible from the low-lying vibrational levels of the electronic ground state.

A bound-state spectrum has been observed by Oppenheimer and Berry [9] in matrix spectra of LiI where matrix-induced changes in potential curves and Franck–Condon factors enable these transitions to be seen. In fig. 3 this situation is schematically illustrated. The part of an upper potential curve that is accessible from the lowest vibrational level of the electronic ground state had already been given by Davidovits and Brodhead [6] and agrees well with a potential curve constructed from the photodissociation cross section in fig. 2 except for a small shift of about 6.5 nm towards shorter wavelengths.

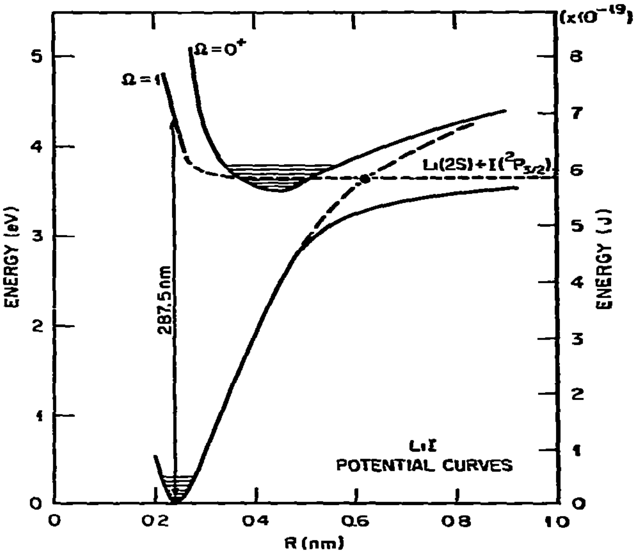

Fig. 3. Schematic illustration of potential energy curves in LiI.

Since we show that this state dissociates, it has to be one with a different symmetry from the ionic ground state; and the first strong UV continuum in LiI is, therefore, due to a perpendicular ($\Pi \leftarrow \Sigma$) transition. In his first analysis, Berry [3] assigned the strong continuum to a parallel transition ($\Sigma \leftarrow \Sigma$); but after Zare and Herschbach [10] had shown in a charge-transfer model for the alkali halides that the transition strength depends on the degree of atomic and ionic mixing, this conclusion had to be questioned [5,9]. Our result shows that the perpendicular transition is indeed favored and therefore helps to clarify this question.

Photodissociation of alkali halides was recently used as an excitation process in alkali-metal resonance line lasers [11]; and since lithium salts were reported to pose special problems [12], this work may be of some interest in connection with those experiments.

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