Photoassociation of cesium atoms into the double minimum $Cs_2\ 3\,^1\Sigma_u^+$ state

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Abstract

We have observed the transition from the free colliding pair of cesium atoms into the outer well of the double minimum $Cs_2\ 3\,^1\Sigma_u^+$ state. This photoassociation process takes place in a cesium vapor consisting predominantly of atoms, in which dimers have been about 85% thermally dissociated. Excellent agreement with quasiclassical simulations was found. We discuss the possibility of using a double minimum $Cs_2\ 3\,^1\Sigma_u^+$ state for the formation of ultracold $Cs_2\ X\,^1\Sigma_g^+$ molecules. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Double minimum states in alkali dimers are always interesting since they can offer the observation of an intriguing spectroscopic quantum interference pattern [1,2].

In connection with ultracold cesium atom collisions it is interesting to investigate a photoassociation excitation process into this outer potential well. Of special interest is the photoassociation into the vibrational–rotational states that lie above or below the potential barrier that divides the two potential wells. Levels just above the barrier can spontaneously radiate at the inner turning point at short internuclear distances and thus, by a vertical transition, end up at the very bottom of the $Cs_2\ X\,^1\Sigma_g^+$ ground state. The levels just below the barrier top could tunnel into the inner potential well. Once in the inner potential well the spontaneous emission at the inner turning point forms $Cs_2\ X\,^1\Sigma_g^+$ ground state molecule, which if formed from an ensemble of ultracold atoms would be translationally ultracold. The tunneling through a potential barrier in the case of the $Cs_2\ 0_g^-$ pure long-range state has been recently discussed in order to explain 'giant' structures in the Cs_2^+ ion signal of the Fioretti et al. experiment [3]. Recently, a great deal of interest has been devoted to the creation of ultracold molecules, and efforts have been devoted to find ways of making ultracold molecules, which cannot be easily cooled by usual two level atomic schemes [4,5]. Photoasso-

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ciation into the outer potential well below the barrier forms a special type of molecule with very large amplitude nuclear vibrations. It is assumed that a molecule in such an elongated state may become very reactive. For example, one could imagine the reaction of such a molecule with H_2 resulting in two CsH molecules, with a large reaction rate coefficient.

Double minimum potential curves are not isolated phenomena in the realm of alkali dimers. It has been shown that both pure long range states, 1_u and 0_g^-, stemming from the $6s\ ^2S_{1/2} + 6p\ ^2P_{3/2}$ asymptote, of Cs_2 are actually double minimum potentials. The outer minima have been observed as the beginning of asymmetry in the atomic spectral line shape [6] and as a pronounced satellite band [7]. They have also been observed quite recently in photoassociation spectra of ultracold cesium in a MOT by Pillet and coworkers [3,8].

However the outer well of all alkali double minimum potentials has never been observed in an absorption process from the dissociating $X\ ^1\Sigma_g^+$ state. We report the first observation of absorption into the outer well of the double minimum $Cs_2\ 3\ ^1\Sigma_u^+$ state.

2. Experiment

We performed absorption measurements using a linear sapphire cell heated to temperatures up to 755°C. We used an absorption setup shown in Fig. 1, which is similar to that described in Ref. [9]. The main part of the setup is an oven with linear ($L = 16$ cm) sealed-off cylindrical all-sapphire cell (ASC) containing 0.6 mg of pure cesium [10]. The temperature was measured by a thermocouple positioned at the middle point of the ASC. Great care was employed when increasing and decreasing the temperature of the oven in order to avoid possible cracks in the walls of the ASC.

The cesium vapor was illuminated by light from a stabilized 150 W halogen lamp. The light passing through the absorption cell was focused on the entrance slit of a 1.5 m Jobin Yvon THR grating spectrometer equipped with a Hamamatsu R936 photomultiplier. The resolution of the monochromator was 0.035 nm (20 μm slit widths). From the
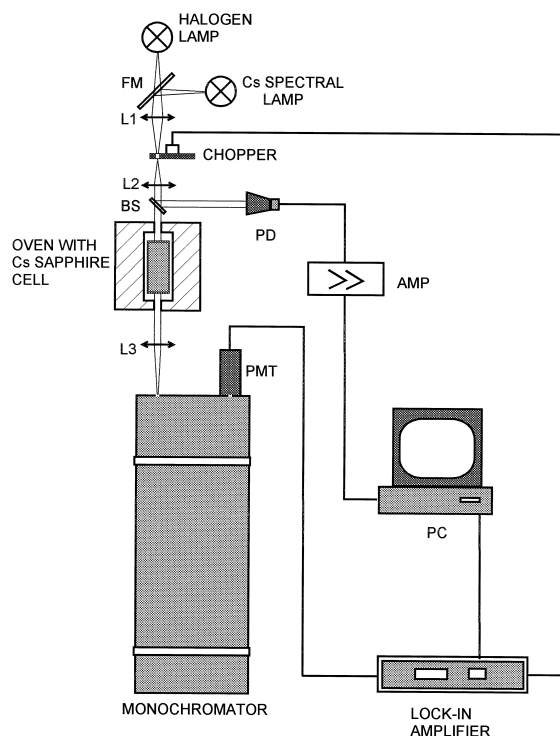

Fig. 1. Experimental setup for absorption measurements. PMT is the photomultiplier, PD the photodiode, FM the folding mirror, BS the beam splitter, AMP the amplifier, PC the personal computer, and L1, L2 and L3 are lenses.

detector the signal was fed into a Stanford Research SR510 lock-in amplifier and stored in a PC. The absorption spectrum was scanned by a rotating holographic grating (1200 grooves/mm) with computer controlled stepper motor.

A low-pressure cesium spectral lamp was used for the absolute wavelength calibration in the region of interest (600–625 nm). For each cesium vapor temperature five independent absorption scans were measured and then averaged.

During the initial heating, saturated cesium vapor appears above the liquid cesium in the ASC. We found by cesium dimer absorption measurements that the maximum density of saturated vapor corresponded to a temperature of about 422°C ($N_{Cs} = 3.5 \times 10^{17}$ cm^{-3} [11]). This is the critical temperature at which all the liquid cesium is evaporated. Therefore at temperatures of the ASC higher than

422°C the cesium atom number density remained constant (it actually slightly increased at the expense of the dimer reduction due to thermal dissociation in the vapor).

3. Results

In Fig. 2 we show the absorption curves at three different temperatures in the wavelength region between 400 and 800 nm, where several cesium atomic and molecular features occur. It can be seen that there are significant temperature dependence for the Cs_2 E ← X, D ← X, C ← X and B ← X absorption bands, because of their bound–bound nature. Due to strong pressure and Doppler broadening together with instrumental broadening of our monochromator the molecular lines of these Cs_2 bound–bound absorption bands are merged and are recorded as a slowly varying continuum. At the highest temperatures, where thermal destruction diminishes bound–bound molecular absorption events, several new absorption bands appear, that are not easily observable at lower temperatures. One of them, peaking at 611.5 nm, coincides with the peak of the interference band of cesium dimer observed in laser induced fluorescence by many researchers [12–14].
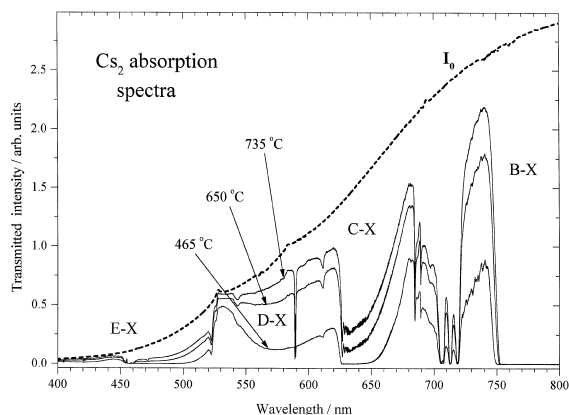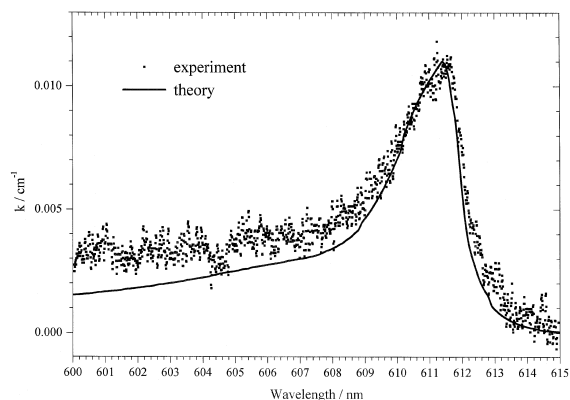

Fig. 3. The measured absorption coefficient of cesium 611.5 nm band (squares) together with a theoretical simulation (solid line).

The absorption coefficient of cesium 611.5 nm band has been measured over a wide range of temperatures (from 420°C to 750°C) at constant cesium atom density, and decreasing number of Cs_2 molecules. By comparing these absorption profiles we established that there was no temperature dependence of the Cs_2 611.5 nm band, the absorption coefficient of the peak of the band at 611.5 nm being equal to 0.011 cm^{-1}. As a consequence of this, we report in Fig. 3 a single absorption coefficient curve for Cs_2 611.5 nm band in the spectral region from 600 to 615 nm. The Cs_2 2(D) $^1\Sigma_u^+$ ← 1(X)$^1\Sigma_g^+$ absorption band, which overlaps Cs_2 band peaking at 611.5 nm, was subtracted under the assumption that the D ← X absorption coefficient could be approximated by the straight line for the spectral region shown in Fig. 3.

Quasiclassical simulation [15] for the Cs_2 611.5 nm band is also shown in Fig. 3 by the solid line. Since there is no theoretical transition dipole moment function $D(R)$ for this transition available, in the present simulation we used a $D(R)$ function taken from Li_2 2$^1\Sigma_u^+$ ← X$^1\Sigma_g^+$ ab initio calculations [16], which is an analogous case of the transition from the ground state to the double-minimum potential. The internuclear distance R is scaled by the factor of 1.483, which is the ratio of the Cs_2 3$^1\Sigma_u^+$ equilibrium distance R_e of the outer well to the Li_2 2$^1\Sigma_u^+$ R_e for the corresponding outer well potential. The absolute value of the $D(R)$ function was

Fig. 2. Absorption spectrum of Cs_2 molecules. The data were taken at 465°C, 650°C and 735°C. The dashed line represents the continuum spectrum of a halogen lamp measured with a cold cell. The spectral regions of the Cs_2 E ← X, D ← X, C ← X and B ← X bands are 440–525 nm, 525–620 nm, 620–685 nm and 750–800 nm, respectively.
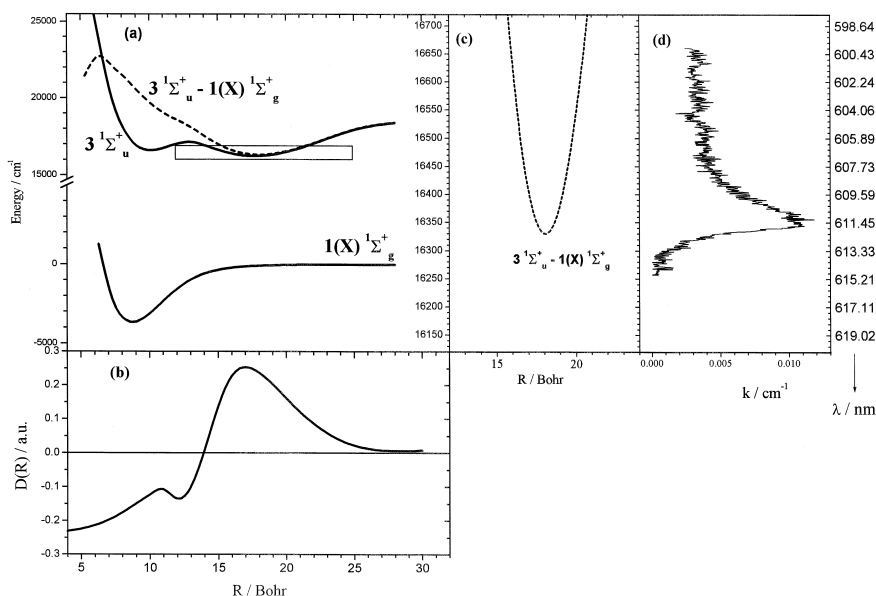
Fig. 4. (a) Potential curves of Cs_2 $1(X)^1\Sigma_g^+$ and $3^1\Sigma_u^+$ states (solid line) together with their difference potential curve (dashed line). (b) Transition dipole moment function $D(R)$ scaled from analogous case of lithium dimer. (c) The part of the Cs_2 $3^1\Sigma_u^+ - 1(X)^1\Sigma_g^+$ difference potential curve enlarged from the box in (a). (d) Experimental absorption coefficient of the Cs_2 611.5 nm band.

adjusted in order to match the absorption coefficient of the measured Cs_2 611.5 nm profile (Fig. 4b).

4. Discussion

Potential curves of Spies and Meyer [17,18] relevant to the Cs_2 611.5 nm band formation are shown in Fig. 4a by a solid line. In Fig. 4b we present the scaled transition dipole moment function adapted from the analogous case of Li_2 dimer. The middle panel (Fig. 4c) shows an enlarged, Cs_2 $3^1\Sigma_u^+ - 1(X)^1\Sigma_g^+$, difference potential curve indicated by the box in the Fig. 4a. On Fig. 4d we replotted the absorption coefficient profile of the Cs_2 611.5 nm band. Note the correspondence of the diffuse band peak with the minimum in the difference potential. A very good agreement between experimental and theoretical results (Fig. 3) indicates the high accuracy of the Cs_2 ab initio potential curves, and that the assumptions about the shape of the transition dipole moment were reasonable. A small discrepancy toward short wavelengths is due to the residual contribution of the Cs_2 $2(D)^1\Sigma_u^+ \leftarrow 1(X)^1\Sigma_g^+$ band [19,20], which has an absorption coefficient maximum at 580 nm.

As the temperature increases the ground state molecule concentration decreases, but the fractional population of the highest vibrational states in the ground electronic state of cesium molecule increases. These highly excited rovibrational states contribute slightly to Cs_2 611.5 nm band at highest temperatures. This small contribution to the band absorption coefficient should slightly increase with increasing temperature. However, we did not observe any temperature dependence and therefore we conclude that the band at 611.5 nm is predominantly a free-bound Cs_2 $3^1\Sigma_u^+ \leftarrow 1(X)^1\Sigma_g^+$ transition. It is essentially a photoassociation of the free colliding pair into the outer minimum of the double minimum Cs_2 $3^1\Sigma_u^+$ potential at internuclear distances of about 18 bohr, which we denote as intermediate long-range distances [21].

Double minimum potentials could in principle be used for making ultracold molecules [22,23] from photoassociation into the outer potential well, with subsequent tunneling through the barrier into the inner well where spontaneous or stimulated emission can create molecule with a very low vibrational and rotational quantum numbers. The reverse tunneling process is in this case less probable because of the

different tunneling probability from the inner well into the outer well. The lighter the alkali molecule the larger the tunneling probability is, and such molecular formation could be expected to be most probable in the case of $^6Li_2$ molecule and somewhat smaller but of the same order of magnitude for the $^7Li_2$ molecules.

5. Conclusion

In the high temperature cesium vapor cell, thermal dissociation enabled the observation of photoassociation leading to the formation of the bound $Cs_2\ 3\ ^1\Sigma_u^+$ molecule in its outer potential minimum. Thermal averaging over the angular momenta and velocity distribution washes out the interference fine structure in the molecular absorption profile, which is usually observed in a single longitudinal mode laser induced fluorescence experiments [14], leaving only the more slowly varying envelope.

If we can find an efficient way how to populate the outer well of $Cs_2\ 3\ ^1\Sigma_u^+$ state, then it may be expected that a tunable laser action would be possible within the 611.5 nm band, since its absorption coefficient is very small. However, due to the large contribution of the overlapping $Cs_2\ 2(D)\ ^1\Sigma_u^+ \leftarrow 1(X)\ ^1\Sigma_g^+$ band absorption this simple molecular laser would be highly unrealistic. Other alkali dimers may be more promising for this type of lasing action if the stimulated emission from the outer minimum of the double minimum potential is not hampered by another overlapping dimer absorption in the same wavelength interval.

Acknowledgements

References

[1] G. Pichler, J.T. Bahns, K.M. Sando, W.C. Stwalley, D.D. Konowalow, L. Li, R.W. Field, W. Müller, Chem. Phys. Lett. 129 (1986) 425.
[2] G. Pichler, S. Milošević, D. Veža, D. Vukičevic, J. Phys. B 16 (1983) 4633.
[3] A. Fioretti, D. Comparat, C. Drag, C. Amiot, O. Dulieu, F. Masnou-Seeuws, P. Pillet, Eur. Phys. J. D 5 (1999) 389.
[4] J.T. Bahns, P.L. Gould, W.C. Stwalley, Adv. At. Mol. Opt. Phys., in press.
[5] W.C. Stwalley, H. Wang, J. Mol. Spectrosc. 195 (1999) 194.
[6] K. Niemax, M. Movre, G. Pichler, J. Phys. B 12 (1979) 3503.
[7] K. Niemax, G. Pichler, J. Phys. B 7 (1974) 2355.
[8] A. Fioretti, D. Comparat, A. Crubellier, O. Dulieu, F. Masnou-Seeuws, P. Pillet, Phys. Rev. Lett. 80 (1998) 4402.
[9] T. Ban, H. Skenderović, R. Beuc, G. Pichler, Europhys. Lett., in press.
[10] D.H. Sarkisyan, A.S. Sarkisyan, A.K. Yalanusyan, Appl. Phys. B 66 (1998) 241.
[11] A.N. Nesmeyanov, Vapor Pressure of Elements, Academic Press, New York, 1963.
[12] H. Kato, K. Yoshihara, J. Chem. Phys. 71 (1979) 1585.
[13] G. Höning, M. Czajkowski, M. Stock, W. Demtröder, J. Chem. Phys. 71 (1979) 2138.
[14] J. Tellinghuisen, G. Pichler, W.L. Snow, M.E. Hillard, R.J. Exton, Chem. Phys. 50 (1980) 313.
[15] R. Beuc, V. Horvatić, J. Phys. B 25 (1992) 1497.
[16] I. Schmidt-Mink, W. Müller, W. Meyer, Technical Report, SFB91, 1984.
[17] N. Spiess, Ph.D. Thesis, University of Kaiserslautern, 1989, unpublished.
[18] W. Meyer, N. Spiess, to be published.
[19] T. Kobayashi, T. Usui, T. Kumauchi, M. Baba, K. Ishikawa, H. Katô, J. Chem. Phys. 98 (1993) 2670.
[20] C. Amiot, W. Demtröder, C.R. Vidal, J. Chem. Phys. 88 (1988) 5265.
[21] O. Dulieu, R. Kosloff, M. Masnou-Seeuws, G. Pichler, J. Chem. Phys. 107 (1997) 10633.
[22] P.S. Julienne, K. Burnett, Y.B. Band, W.C. Stwalley, Phys. Rev. A 58 (1998) R797.
[23] J. Javanainen, M. Mackie, Phys. Rev. A 58 (1998) R789.