J. Phys. Chem. A **2001,** *105,* 2225−2227

Electron-Impact Spectroscopy Investigation of Diketene†

I. M. Xavier, Jr.,*,‡ K. N. Walzl,§ and M. R. Giorgi||

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology,
Pasadena, California 91125

Received: September 17, 2000; In Final Form: November 7, 2000

The electronic spectrum of diketene was investigated by the technique of variable-angle, electron energy loss spectroscopy, using the impact energies of 25 and 50 eV, and varying the scattering angle from 10° to 90°. Transitions have been observed at 4.36, 5.89, 6.88, and 7.84 eV. On the basis of the intensity variation of these transitions with impact energy and scattering angle, and through analogy with simpler molecules, the first three are tentatively assigned to an $n \rightarrow \pi^*$ transition, a $\pi \rightarrow \sigma^*(3s)$ Rydberg transition, and a $\pi \rightarrow \pi^*$ transition.

I. Introduction

Electron-impact spectroscopy has been employed to study electronic transitions in a wide variety of molecules,[1,2] and the measured differential cross sections have been utilized to aid in assignment of transitions.[3−5] In this work, low-energy variable-angle electron-impact spectroscopy has been used to investigate both optically forbidden and optically allowed electronic transitions in the spectrum of diketene. Previous optical studies[6,7] of diketene in solution extended to 250 nm (about 5 eV) and showed only a weak, ultraviolet, absorption band at 313 nm (3.96 eV). The present gas-phase work shows four new, higher energy loss, electronic transitions including a spin-forbidden one. The diketene (4-methyleneoxetan-2-one) structure[8,9] was elucidated by X-ray diffraction[10] in 1952, 45 years after its first preparation. The planarity of the four-membered ring has been established by Raman spectroscopy.[11] Recently, infrared and Raman spectra of diketene have been investigated theoretically by quantum chemistry methods.[12]

Information about the nature of the excited electronic states observed in an electron-impact spectrum can be obtained by studying the dependence of the intensity of each transition on impact energy and scattering angle.[13,14] Transitions which in optical spectroscopy are both electric-dipole-allowed and spin-allowed have differential cross sections (DCS) in electron-impact spectroscopy which are forward-peaked.[13,14] In contrast, spin-forbidden transitions involving changes in the molecular spin quantum number by ±1, such as singlet → triplet excitation, have more nearly isotropic DCS in the angular range 10°−90°.[13,14] Such transitions occur by the mechanism of electron exchange.[15] Spin-allowed but electric-dipole-forbidden processes are forward-peaked, but often not as much as fully allowed transitions.[16,17] As reflected in the different DCS shapes, the optically forbidden processes, and in particular the spin-forbidden ones, become more intense with respect to the optically allowed processes at large scattering angles.[13,14] Another advantage of the electron-impact method is that spectral features in the far ultraviolet are as easily examined as those in the visible and near-ultraviolet.

II. Experimental Section

The electron spectrometer used in this study was similar to one described previously.[18] Briefly, an electron beam is energy-selected by a hemispherical electrostatic energy analyzer (and the associated focusing lenses) and scattered from the target vapor in a scattering box. In this work, the incident-beam current was between 1and 10 nA and was typically 4 nA. Sample pressures were estimated to be between 5 and 10 mTorr. Electron-energy losses were determined at angles between 10° and 90° by means of a second electrostatic energy analyzer and detector. The energy-loss spectrum thus obtained is analogous to an optical absorption spectrum, except that optically forbidden processes are much more readily detected.[13,14]

The spectrometer resolution (as measured by the full width at half-maximum of the elastically scattered feature) varied between 50 and 100 meV for all reported spectra and was typically 80 meV. Diketene was obtained from Aldrich, and had a stated purity of 98%. All samples were subjected to three liquid nitrogen freeze−pump−thaw cycles and used without further purification.

III. Results and Discussion

Figure 1 shows the low energy loss portion of the diketene electron-impact spectrum at (a) $E_0 = 50$ eV, $\theta = 10°$; (b) $E_0 = 50$ eV, $\theta = 90°$; (c) $E_0 = 25$ eV, $\theta = 10°$; and (d) $E_0 = 25$ eV, $\theta = 90°$. These figures indicate the presence of four transitions having maximum intensities at 4.36, 5.89, 6.88, and 7.84 eV energy loss. In Figure 2 we display the corresponding differential cross-section curves at the impact energies of 25 and 50 eV, obtained by a method previously described.[16]

The most intense feature has a peak intensity at 6.88 eV. From Figure 2 the elastic peak and the peak at 6.88 eV exhibit an intensity variation of about 2 orders of magnitude over the angular range, indicative of fully allowed bands. The transitions at 7.84 and 5.89 eV have DCS curves less forward-peaked, but they can still be considered as allowed bands. The DCS of the

---

† Part of the special issue “Aron Kuppermann Festschrift”. Contribution No. 8589 from the Arthur Amos Noyes Laboratory of Chemical Physics.

* Corresponding author. Present address : Department of Statistics, Federal University of Pernambuco, 50670-901 Recife, PE, Brazil.

‡ Work performed in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at the California Institute of Technology.

§ Present address: Institute for Defense Analyses, 1801 N. Beauregard Street, Alexandria, VA 22311-1772.

|| Present address: Intel Corporation, AL3-17, 5200 N. E. Elam Young Parkway, Hillsboro, OR 97124.

10.1021/jp003335b CCC: $20.00

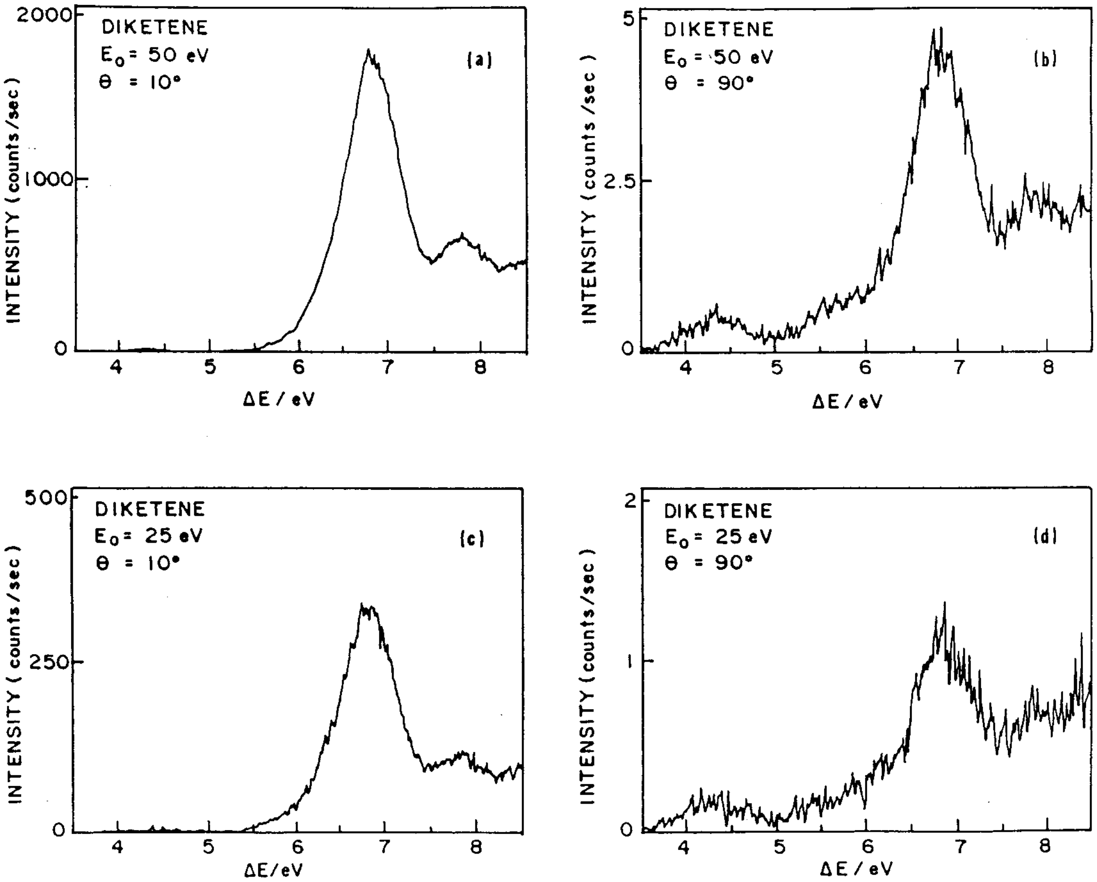

Figure 1. Diketene electron energy loss spectra at (a) $E_0 = 50$ eV, $\theta = 10°$; (b) $E_0 = 50$ eV, $\theta = 90°$; (c) $E_0 = 25$ eV, $\theta = 10°$; and (d) $E_0 = 25$ eV, $\theta = 90°$.

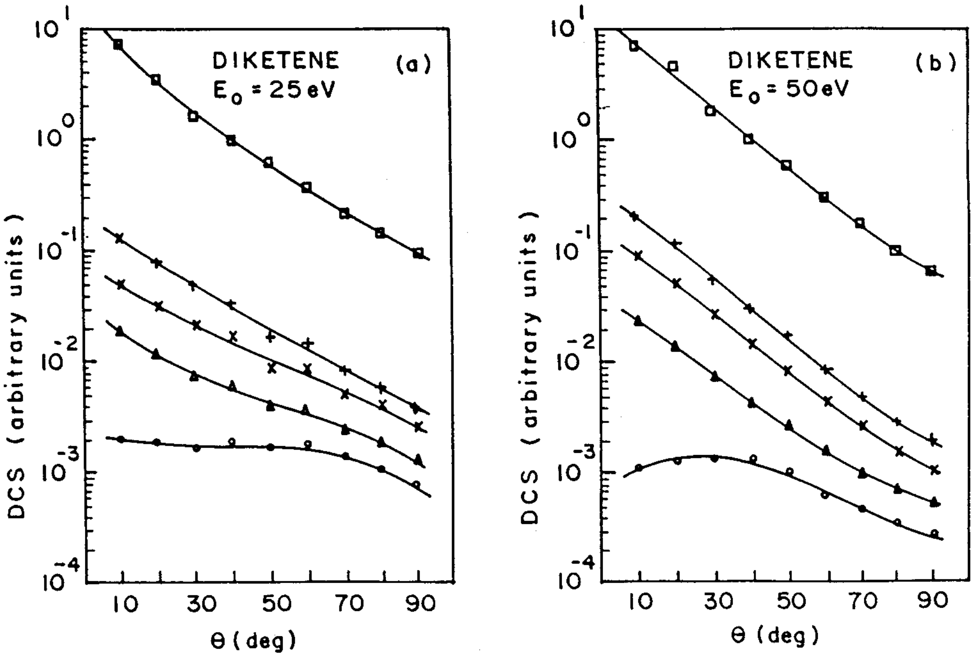

Figure 2. Differential cross sections of diketene at (a) $E_0 = 50$ eV and (b) $E_0 = 25$ eV. Elastic scattering (□) and transitions to the excited states lying at 4.36 (○), 5.89 (△), 6.88 (+), and 7.84 eV (×) above the ground state.

4.36 eV transition is nearly isotropic and has the characteristic behavior of a spin-forbidden transition.[13,19]

Until now, no far-ultraviolet spectra of diketene have been reported. In the absence of any calculations directly relevant to the electronic spectroscopy of this molecule, we are tentatively assigning these observed transitions of diketene under the qualitative assumptions described below. The weak ultraviolet transition observed in earlier optical studies of diketene in solution is not observed in our spectra, and cannot be justified by these simple arguments.

Diketene contains two important chromophores: the carbonyl and the ethylene groups. The carbonyl in small monoketones exhibits the well-known (n, π^*) band in the ultraviolet followed by three Rydberg bands (n, (3s, 3p, 3d)) in the far-ultraviolet.[20]

The (π, π^*) band is expected to be at relatively high energy loss (possibly as high as 9.0 eV) superimposed by Rydberg bands.[20,21] The carbon−carbon double bond in monoalkenes exhibits an intense (π, π^*) absorption band, which coincides with, or is preceded by, a (π, 3s) Rydberg band.[20] In ethylene itself, the Rydberg band is superimposed on the low-frequency wing of the (π, π^*) band,[22] while in highly methylated or fluorinated olefins, the Rydberg (π, 3s) becomes the first spectral band and is well separated from the (π, π^*) band.[20]

The observed spectral bands of diketene can be tentatively assigned by analogy to the properties of the isolated carbonyl and ethylene chromophores. The following peak assignments are suggested, although it is likely that the observed peaks consist of several overlapping bands. In the energy-loss range of this work (3.5−8.5 eV), the spin-forbidden transition at 4.36 eV is the only spectral feature that can be attributed to the carbonyl chromophore. By analogy with previous electron-impact assignments in monoketones,[21,23] this transition is assigned as $n \rightarrow \pi^*$(S−T). The other three spin-allowed transitions can be attributed as due to mainly the carbon−carbon, double-bond chromophore. The strongest transition at 6.88 eV is assigned as $\pi \rightarrow \pi^*$(S−S), based on the electron energy-loss spectroscopy of methyl-substituted ethylenes[24] and fluoroethylenes.[25] The shoulder at 5.89 eV resembles the shoulder on the strongest feature in the energy-loss spectrum of the fluoroethylenes[25] and is assigned as $\pi \rightarrow \sigma^*$(3s) Rydberg (S−S). Finally, the spin-allowed band at 7.84 eV is probably another Rydberg band, similar to those observed in ethylenes.[22]

IV. Summary

In conclusion, we have used the method of low-energy, variable-angle, electron-impact spectroscopy to study the far-ultraviolet spectrum of diketene. Four new transitions have been observed, including one that is spin-forbidden. Tentative assignments of these transitions were made under qualitative assumptions. We hope that calculations will be available soon in order to confirm these assignments.

Acknowledgment. This work was supported in part by the U.S. Department of Energy, Contract No. DE-AM03-76F00767, Project Agreement No. DE-AT03-76ER72004.

References and Notes

(1) Gianturco, F. A.; Jain, A. *Phys. Rep*. **1986**, *143*, 348.

(2) Morrison, M. A. *Adv. At. Mol. Phys*. **1988**, *24*, 51.

(3) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1974; Vols. 1 and 2.

(4) Lassetre, E. N.; Skerbele, A.; Dillon, M. A.; Ross, K. J. *J. Chem. Phys*. **1968**, *48*, 5066.

(5) Trajmar, S.; Register, D. F.; Chutjian, A. *Phys. Rep*. **1983**, *97*, 219.

(6) Roberts, J. D.; Armstrong, R.; Trimble, R. F.; Burg, M. *J. Am. Chem. Soc*. **1949**, *71*, 843.

(7) Calvin, M.; Magel, T. T.; Hurd, C. D. *J. Am. Chem. Soc*. **1941**, *63*, 2174.

(8) Clemens, R. J. *Chem. Rev*. **1986**, *86*, 241.

(9) (a) Seidl, E. T.; Schaefer, H. F., III. *J. Am. Chem. Soc*. **1990**, *112*, 1493. (b) Seidl, E. T.; Schaefer, H. F., III. *J. Phys. Chem*. **1992**, *96*, 657.

(10) Katz, L.; Lipscomb, W. N. *J. Org. Chem*. **1952**, *17*, 515.

(11) Durig, J. R.; Willis, J. N., Jr. *Spectrochim. Acta* **1966**, *22*, 1299.

(12) Dobrowolski, J. C.; Jamroz, M. H.; Borowiak, M. A.; Quaranta, E.; Aresta, M. *Vib. Spectrosc*. **2000**, *22*, 19.

(13) Kuppermann, A.; Rice, J. K.; Trajmar, S. *J. Chem. Phys*. **1968**, *72*, 3094.

(14) Trajmar, S.; Rice, J. K.; Kuppermann, A. *Adv. Chem. Phys*. **1970**, *18*, 15.

(15) Oppenheimer, J. R. *Phys. Rev*. **1927**, *29*, 433.

(16) Mosher, O. A.; Flicker, W. M.; Kuppermann, A. *J. Chem. Phys*. **1975**, *62*, 2600.

(17) Cartwright, D. C.; Hunt, W. J.; Williams, W.; Trajmar, S.; Goddard, W. A., III. *Phys. Rev*. **1973**, *A8*, 2436.

(18) (a) Koerting, C. F.; Walzl, K. N.; Kuppermann, A. *Chem. Phys. Lett*. **1984**, *109*, 140. (b) Koerting, C. F. Ph.D. Thesis, California Institute of Technology, Pasadena, 1985.

(19) Kuppermann, A.; Flicker, W. M.; Mosher, O. A. *Chem. Rev*. **1979**, *79*, 77.

(20) Sandorfy, C.; Lussier, L. S In *Photophysics and Photochemistry in the Vacuum Ultraviolet*; McGlynn, S. P., Findley, G. L., Huebner, R. H., Eds.; Reidel: Dordrecht 1985; p 819.

(21) Walzl, K. N.; Koerting, C. F.; Kuppermann, A. *J. Chem. Phys*. **1987**, *87*, 3796.

(22) Merer, A. J.; Mulliken, R. S. *Chem. Rev*. **1969**, *69*, 639.

(23) Frueholtz, R. P.; Flicker, W. M.; Kuppermann, A. *Chem. Phys. Lett*. **1976**, *38*, 57.

(24) Flicker, W. M.; Mosher, O. A.; Kuppermann, A. *Chem. Phys. Lett*. **1975**, *36*, 56.

(25) Coggiola, M. J.; Mosher, O. A.; Flicker, W. M.; Kuppermann, A. *Chem. Phys. Lett*. **1974**, *27*, 14.