

TABLE I. Raman frequencies (cm^{-1}) for molten carbonate-containing systems.^a

Sample	Temp (°C)	ν_1	ν_3	ν_4
$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ (42-27-31 mole %) ^b	400	1064±2	1362-1475	700±2
$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (59-41 mole %) ^c	500	1066±2	1372-1496	697±2
$\text{Li}_2\text{CO}_3\text{-LiBr}$ (13-87 mole %) ^d	500	1080±2

^a See Footnotes b-d for the phase-diagram studies.

^b G. J. Janz and M. R. Lorenz, *J. Chem. Eng. Data* **6**, 321 (1961); M. Rolin and J. M. Recapet, *Bull. Soc. Chim. France* **1964**, 2110.

^c N. A. Reshetnikov and O. G. Perfilova, *Zh. Neorg. Khim.* **13**, 1662 (1968).

^d D. S. Lesnykh and E. P. Carmatina, *Zh. Neorg. Khim.* **12**, 1367 (1967).

(13 mole %)-LiBr (87 mole %) eutectic, are given in Table I along with the results for the $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ melt.

The data presented here for the molten carbonates bear some resemblance to the results obtained previously for molten nitrates. The frequency of ν_1 for nitrate ion was found to increase with increasing polarizing power of the cation environment in molten nitrates.^{6,9} A similar frequency shift of the ν_1 vibration with change in polarizing power is evident for carbonate ion from the data in Table I. For the $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ and $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ melts, which should have cation environments of nearly equivalent polarizing power, the ν_1 vibration is observed at 1064 and 1066 cm^{-1} , respectively, whereas for the $\text{Li}_2\text{CO}_3\text{-LiBr}$ eutectic, which has a cation environment of significantly greater polarizing power due to the large excess of lithium ion relative to carbonate ion, the ν_1 frequency is at 1080 cm^{-1} . Admittedly, this comparison assumes that the effect of the presence of bromide is inconsequential. In this regard, Janz and Kozlowski⁸ found that in $\text{NaNO}_3\text{-NaCl}$ and $\text{NaNO}_3\text{-NaBr}$ melts, the ν_1 frequency remains essentially unchanged as the composition of the respective halide is varied.

Splitting of the degenerate modes ν_3 and ν_4 (particularly ν_3) has also been observed in molten nitrates as a consequence of environmental perturbation. Although the signal strengths of ν_3 and ν_4 for CO_3^{2-} have been weak, we do observe the shoulder on ν_4 for the $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ melts repeatedly and in several of our spectra of this melt, we have observed what appears to be splitting of ν_3 as shown in Fig. 1(a). The band envelope of ν_1 for CO_3^{2-} was found to be symmetric in all three cases.¹⁰

* Work performed under auspices of the U.S. Atomic Energy Commission.

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¹⁰ G. J. Janz has confirmed the symmetry of ν_1 in the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ system in a private communication.

Threshold Behavior for Photo Double Ionization*

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(Received 7 January 1970)

There has been considerable interest in the nature of threshold laws in ionization processes; for example, it is important to know threshold behavior when interpreting experimental data obtained in impact experiments. A number of authors have theoretically investigated the problem¹⁻⁴ and have found that the probability of ionization should be independent of the method of formation and depend only on the long-range forces of the products leaving the collision zone. Results of the theoretical treatments vary in details, but for two electrons leaving the collision zone from a singly charged ion, the threshold law is thought to be approximately linear with energy,⁵ and the energy interval in which the cross section is linear is uncertain. Photo double ionization would then be expected to have the same threshold behavior as single ionization by electron impact. This relationship has not been experimentally studied although photo double ionization processes have been reported in the literature.⁶

The direct measurement of the ionization process enables a determination of the ionization potential of the ion, provided the ionization potential of the neutral is known.

This work was undertaken to study the photo double ionization process in ytterbium in order to determine threshold behavior of the ionization cross section and the double ionization potential of ytterbium. The ionization potential of Yb(II) is given by Meggers⁷ from extrapolation of three members of a Rydberg series as 12.17 eV. From spectroscopic⁸ and photo-ionization⁹ studies the ionization potential of Yb(I) is 6.25 eV, thus the double ionization potential is 18.42 eV.

The experimental apparatus used was described earlier.¹⁰ A ytterbium atomic beam was generated with a Knudsen cell and crossed with a photon beam in the source of the mass spectrometer. Radiation from the helium molecular continuum was passed through the monochromator which had a bandpass of 5 Å. The

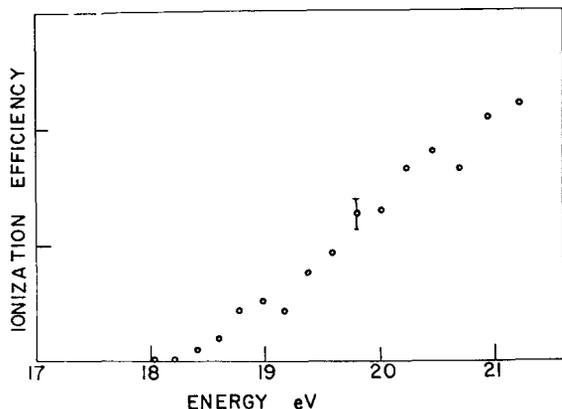


FIG. 1. Photoionization efficiency curve for double ionization of ytterbium. The horizontal scale is energy in electron volts. The vertical scale is in arbitrary units.

photon intensity was monitored by monitoring photoelectrons from an inconel surface that had been calibrated against a sodium salicylate coated photomultiplier.

Figure 1 shows the ionization efficiency curve for the double ionization process in ytterbium. Within the precision of the measurement, the curve rises linearly from onset at 18.35 ± 0.10 eV. Using 6.25 eV for the ionization potential of Yb(I), we derive the ionization potential of Yb(II) to be 12.11 ± 0.10 eV. This, within experimental error, is the value reported by Meggers. The linear nature of the ionization efficiency curve is in agreement with the prediction of an approximately linear cross section when two electrons leave the collision zone. At 21.23 eV, the ratio of single ionization to double ionization is about 15:1.

* This work was supported in part by a grant from the National Science Foundation and in part by the Advance Research Projects Agency.

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Deuterium Quadrupole Coupling Constants in Nitrobenzenes*

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(Received 18 December 1969)

In a recent report on the calculation of deuterium quadrupole coupling constants in deuterocarbons,¹ we

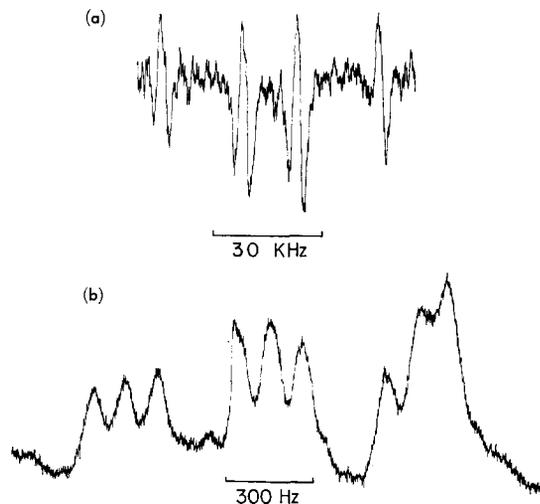
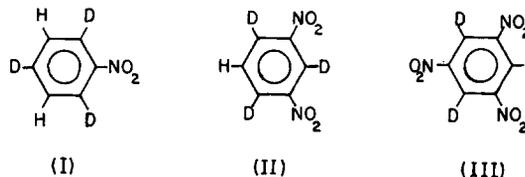


FIG. 1. NMR spectra of nitrobenzene-2,4,6- d_3 in a liquid crystal solution at 25°C. The composition of the solution (in mole fraction) was 0.60 butyl-*p*-(*p*-ethoxyphenoxy) carbonyl phenyl carbonate, 0.20 *p*-(*p*-ethoxyphenylazo) phenylheptanoate, and 0.20 nitrobenzene-2,4,6- d_3 . (a) Deuteron resonance at 8.0 MHz, derivative of dispersion mode. (b) Proton resonance at 100 MHz.

have pointed out that electron-withdrawing substituents would reduce the quadrupole coupling constant of deuterium bonded to a carbon atom. This has been borne out by systematic experimental data for substituted alkanes.^{2,3} We now wish to report a similar result for nitrobenzenes.

The measurement of deuterium and proton NMR in liquid crystal solutions has proved to be a convenient way of obtaining deuterium quadrupole coupling constants.³⁻⁵ For that purpose, the deuterium and proton NMR spectra of nitrobenzene-2,4,6- d_3 (I),⁶ 1,3-dinitrobenzene-2,4,6- d_3 (II),⁷ 1,3,5-trinitrobenzene, and 1,3,5-trinitrobenzene- d_3 (III)⁸



were taken in liquid crystal solutions. The experimental conditions have been described previously.⁵ The spectra of (I) are shown in Fig. 1. The two pairs of peaks in the deuterium resonance spectrum in Fig. 1(a) arise from the quadrupole splittings of the meta- and para-deuterons in (I). The deuterium NMR spectra of (II) and (III) show similar quadrupole splittings ($\Delta\nu_Q$), the values of which are listed in Table I. The proton resonance spectrum for I [Fig. 1(b)] is "first order" and can be readily analyzed by inspection. The dipole-dipole interactions between 2-D and 3-H, and between 5-H and 6-D, split the proton signal into a large triplet. The smaller triplet is due to the dipolar splitting of the 3- and 5-protons by the deuterium at the 4 position.