Irradiation of benzene molecules by ion-induced and light-induced intense fields

D. Mathur
Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India
(Received 16 August 2000; published 6 February 2001)

The correspondence between intense ion-induced and laser-induced fields is explored in terms of magnitude and the temporal, directional, and spatial properties of the two types of field. Irradiation of benzene by these fields yields similar ionization patterns, indicating that whether the intense field is of picosecond or attosecond duration is of little consequence to the ionization dynamics.

DOI: 10.1103/PhysRevA.63.032502 PACS number(s): 33.80.−b, 33.90.+h, 34.90.+q, 33.15.Ta

I. INTRODUCTION

Matter is inherently unstable when exposed to electric fields whose magnitudes approximate interatomic Coulombic fields. Studies of the response of matter to very intense fields address fundamental issues concerning the physics of systems driven strongly away from equilibrium. There are two approaches that enable terrestrial access to such fields, and their use in probing the ionization (and dissociation) dynamics of atoms (and molecules): (a) use of fast, highly charged ions, and (b) intense laser light. Much work has recently been carried out on ionization dynamics in both accelerator- and laser-based experiments [1,2], but explorations of the crucial aspect that both approaches give rise to intense, short-duration *fields* (and it is such fields that determine the overall dynamics) have been desultory.

The interaction of atoms and molecules with intense fields is a complex, nonperturbative, dynamical problem, and prospects of rigorous theoretical treatment remain remote. Exploring the similarities and differences between laser-induced and ion-induced intense fields is strategically important if an understanding is to develop of the dynamics governing the behavior of matter in strong fields. The parameters of importance are the magnitudes, directional properties, and time durations of the fields, and their effects on atomic and molecular dynamics. It is useful to consider two facets of intense field interactions: time dependence and structure dependence. Experimental exploration of both these facets, albeit initially morphological, is clearly important. Specifically, it is necessary to identify a class of target species whose properties make them suitable for studies aimed at disentangling the effects of the two facets so that prospects of developing improved insight are improved.

The time-dependent aspect of the field-target interaction is especially of relevance to molecules. Contemporary laser technology makes available intense light fields in pulses of picosecond and femtosecond duration. For molecules, these time scales are significant in relation to typical rotational and vibrational time periods (tens of picoseconds and tens of femtoseconds, respectively). In the case of ion-induced fields, however, a beam of highly charged ions traverses a distance of only a few angstroms in tens of attoseconds, thereby probing molecular dynamics on times scales in which all internal degrees of freedom are ''frozen.'' Moreover, these ultrashort times imply enormous uncertainties in energies, allowing molecular dynamics to be studied outside the ambit of conventional quantum mechanics.

The earliest explorations of the *correspondence* between ion-induced and laser-induced intense fields, and their effects on molecular dynamics, were initiated by Boyer *et al.* [3] who studied the ionization properties of triatomics like CO_2. Subsequent work focused on similarities and differences between ion-induced and laser-induced ionization patterns in more complex molecules [4]. In the case of H_2O, the morphology of the ionization pattern was found to be grossly different for the two types of field of otherwise similar magnitude. Differences in a series of chloromethanes of different symmetries were much less, but were still significant. These differences could be rationalized by noting that, although the magnitudes of the ion-induced and light-induced fields were almost identical in these experiments, their directional properties were different in the following sense: the laser light was linearly polarized and so the direction of the field vector was constant in the course of the interaction, unlike the time dependence that is intrinsic to the direction of the ion-induced field. Some evidence was also found that, for laser-molecule interactions, the directional properties of the applied field can influence molecular dissociation pathways [5]. Other factors, such as indirect ionization events (involving intermediate electron capture and loss) in the ion-impact case, were discounted by judicious choice of experimental conditions.

Removal of a major block in attempts to develop insights into the correspondence between ion-induced and laser-induced strong fields and to explicitly explore the time-dependent aspects of strong field-molecule interactions would be to locate a molecular target that yields almost the same ionization pattern in the two fields. A noteworthy feature of all the molecules that have been used as targets in earlier studies is that their quantal properties (specifically of the highest occupied molecular orbitals) yielded spatially anisotropic ground-state electronic charge density distributions. We report here results of a study that identifies benzene, with its ''sea'' of delocalized valence π electrons, as a target with a fairly isotropic charge distribution that might facilitate establishment of the correspondence between intense ion-induced and laser-light-induced fields in probes of the ionization dynamics in temporal regimes spanning the attosecond and picosecond ranges. We also show that, although the temporal properties of the two types of field are so different, the spatial properties have marked similarities.

The correspondence between the two types of field is most usefully established by considering three temporal regimes. In the case of relativistic ion beams (whose energy

$\sim$GeV/nucleon, $\beta = v/c \sim 1$) colliding with molecules, the Weizsäcker-Williams equivalent photon model [6] transforms the Coulombic field in the projectile's rest frame to the target's rest frame, and equates the effect of the field to two orthogonally directed photon pulses. Application of such equivalent photon pulses to atomic ionization has recently attracted attention [7]. At the opposite temporal extreme, pure electrostatics (Coulomb's law) tells us that, for example, Si^{3+} projectiles produce a field of ~ 5 V Å^{-1} (~ 0.1 a.u.) at a target atom that is 3 Å away. In the intermediate regime, one that is experimentally most accessible using accelerators, the effective ion-induced electric field experienced by a target may be deduced from the Poynting vector: $I_{eff}(t) = (1/\mu_0)|\vec{E}(t) \times \vec{B}(t)|$.

II. COMPARING ION-INDUCED AND LIGHT-INDUCED FIELDS

Our ion-impact experiments used fast beams of mass-selected, highly charged ions (Si^{q+}, $q = 3$, 8, and F^{7+}, at energies of 50–110 MeV) that were obtained from a tandem accelerator. Slow recoil ions resulting from large impact-parameter interactions between the projectiles and C_6H_6 vapor were extracted, with unit collection efficiency, into either a linear time-of-flight (TOF) spectrometer or a quadrupole mass filter located orthogonally to the incident ion beam using previously described methodology [4].

In the laser experiments, light pulses (of 35 ps and 100 fs duration) from high-intensity Nd:YAG (yttrium aluminum garnet) and Ti:sapphire lasers were focused by a 10 cm biconvex lens such that peak intensities within the focal volume were in the range 10^{12}–10^{16} W cm^{-2}. Ions produced in the focal volume were extracted, again at 90° to the laser beam, and analyzed by a two-field TOF setup.

One important facet of the comparison of ion-induced and light-induced ionization dynamics is the quantification of the peak magnitude of the applied field. A limiting value of the impact parameter b has to be deduced for each ion-collision system. Although b is a somewhat elusive parameter for molecular targets, the range of b values that come into play manifests itself in the mean recoil energy (E_r) that is imparted to each molecular ion that is created in the interaction. This, in turn, is reflected in the temporal width of molecular ion peaks in the measured TOF spectrum. In the case of $C_6H_6^+$ ions formed with Si^{q+} ($q = 3$,8) projectiles, we measured E_r to lie in the range 30–40 meV. There is an established method [8], based on classical trajectory Monte Carlo techniques [9], that enables deductions to be made of the impact-parameter dependence of multiple ionization probabilities in fast-ion collisions. A value of 3 Å was deduced as the lower limit for b in our experiments. Collisions that occur at smaller b values give rise to recoil energies far in excess of E_r, and these are discriminated against by the angular resolution of the spectrometers used by us.

We confirmed the veracity of our deductions of b by determining total cross sections for formation of low-energy Ar^{q+} recoils ($q = 1$–10) in the same apparatus. Deduction of b can also be complicated by electron capture and loss processes that might influence the formation of recoils in charge state $q > 1$. However, it was confirmed that for a range of ions (namely, Si^{q+}, $q = 3$–12), direct ionization dominated the overall dynamics. By way of example, the measured total cross section for Ar^{4+} formation in Si^{10+}-Ar collisions was 8×10^{-17} cm^2 while cross sections for Ar^{4+} formation accompanied by one-electron capture and loss were 3×10^{-18} cm^2 and 7×10^{-19} cm^2, respectively. For C_6H_6-ion collisions at 50–110 MeV, the domination of direct ionization processes is likely to be even more pronounced.

In laser experiments, determination of the peak field value is somewhat less difficult, but note the following facet that has hitherto not been articulated. Just as the ion-C_6H_6 interaction accesses a range of b values ($b > 3$ Å), and, hence, exposes the molecules in the interaction zone to a corresponding range of applied fields, so in the laser case there is a spatial distribution of intensities that gives rise to a corresponding distribution of fields. The spatial distribution in the laser case is a consequence of the spatial focusing that produces high-energy light pulses. Consequently, in ionization studies using intense lasers, the target invariably experiences significant spatial and temporal variations in the laser intensity. The situation is complicated because different intensity intervals occupy different volumes within the laser-molecule interaction zone that is sampled by the TOF spectrometer. The lower intensities occupy a much larger volume as compared to the spatial region over which the peak laser intensity acts. The experimental signal that results from laser-molecule interactions is, therefore, a measure of intensity/volume-integrated effects that are averaged over inhomogeneities in the ion distribution in the focal region. Such spatial distribution of the laser-induced field, and the ion distribution that results from it, was measured using a method that has recently been described in detail [10].

The similarities with impact-parameter-dependent fields that are generated in ion-molecule interactions now become obvious. In the latter case also there is a range of impact parameters that come into play in determining the ion-induced ionization dynamics, with large impact parameters (lower field intensities) playing a dominant role. The spatial field distributions obtained in both the ion-impact and laser-based experiments are shown in Figs. 1 and 2, respectively. We express the field magnitude obtained using ions in terms of an effective intensity. This is useful in that direct comparison of ion-induced field magnitudes can be made with an easily determined parameter in the laser experiments, namely, the light intensity. We recall that the electric field E (in V cm^{-1}) and light intensity I (in W cm^{-2}) are related by $I = 1.33 \times 10^{-3} E^2$. A field of about 10^9 V cm^{-1} thus implies an effective intensity of 10^{15} W cm^{-2}. Judicious choice of operating conditions enables the spatial field distributions to be very similar in the two sets of experiments. The examples shown are for a 100 MeV beam of Si^{8+} ions, readily accessed in tandem accelerators, and for a 100 fs long laser pulse of peak intensity 2×10^{15} W cm^{-2}, accessed by focusing a 1 mJ beam of 806 nm wavelength from a Ti:sapphire laser to a spot size of ~ 25 μm.

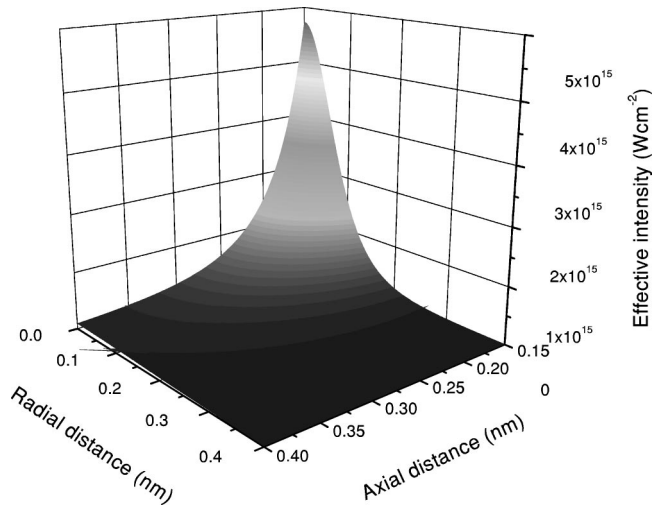

FIG. 1. The radial and axial distribution of applied field within the interaction volume for Si^{8+}-C_6H_6 collisions. The magnitude of the field is expressed in terms of an effective intensity in order to aid comparison with the equivalent distribution pattern obtained in laser-C_6H_6 interactions.

III. RESULTS AND DISCUSSION

A. Ionization and fragmentation patterns

Figure 3 shows typical ionic fragmentation patterns obtained when C_6H_6 is irradiated by 100 MeV Si^{3+} ions and 35 ps long laser pulses of 532 nm wavelength. The peak intensity in the latter case was $\sim 8\times10^{13}$ W cm^{-2} and, by using a small (2 mm) aperture at the entrance of our TOF spectrometer, the lower part of the intensity range that we accessed was $\sim 5\times10^{12}$ W cm^{-2}. For the ion-impact data, the peak value of effective intensity at an impact parameter of 3 Å was $\sim 5\times10^{14}$ W cm^{-2}. We also conducted experiments with Si^{8+} and F^{7+} ions, and with 100 fs duration laser

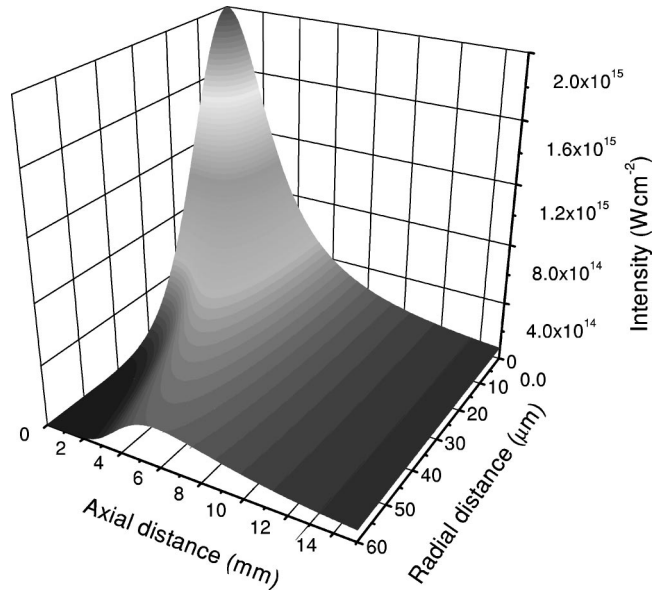

FIG. 2. The spatial distribution of applied field within the focal volume for laser-C_6H_6 interactions (see text).

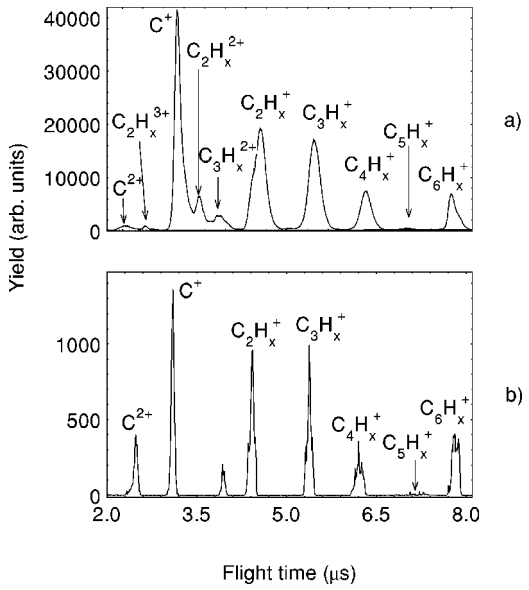

FIG. 3. Ion fragmentation patterns obtained upon irradiation of C_6H_6 by (a) 100 MeV Si^{3+} ions (similar patterns were obtained using Si^{8+} and F^{7+} ions), and (b) 35 ps long laser pulses of 532 nm wavelength and peak intensity of 8×10^{13} W cm^{-2}.

pulses (of 806 nm wavelength), with peak intensities in the range 10^{13}–(5×10^{16}) W cm^{-2}. The gross features of the measured ionic fragmentation patterns remained essentially unaltered, although the highest laser intensities gave rise to a larger degree of multiple ionization (which could also be directly correlated with ion beam data).

Illustrative data are shown in Fig. 4 for 110 MeV Si^{8+}

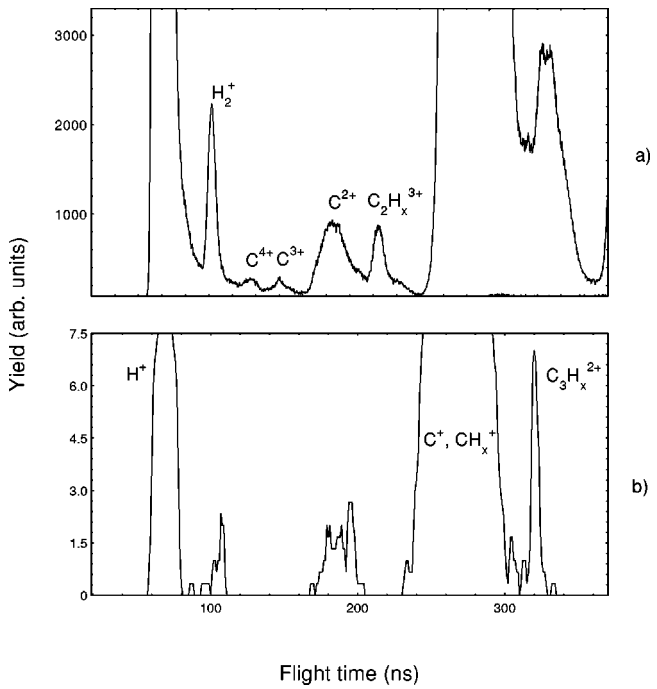

FIG. 4. Fragmentation of C_6H_6 by (a) 110 MeV Si^{8+} ions and (b) 100 fs long laser pulses of 806 nm wavelength and peak intensity of 5×10^{15} W cm^{-2}.

impact and irradiation by 100 fs laser pulses of intensity 5×10^{15} W cm^{-2}. Here, a larger (15 mm) aperture was used at the entrance of our TOF spectrometer in the laser experiments, thereby giving access to the entire intensity range shown in Fig. 2. Under these circumstances, the contribution of the parent $C_6H_6^+$ ion to the mass spectrum is very much enhanced (not shown in the figure). The central portion of the focal volume samples the peak intensity region and, consequently, multiple ionization events are more evident (Fig. 4). A noteworthy feature is the unexpected preponderance of H^+ and H_2^+ fragments, indicating that very energetic processes occur in this intensity regime which overcome the intrinsic strength of the aromatic ring structure, causing extensive fragmentation and opening dissociation channels that are seldom accessed in electron impact experiments. We refrain from discussing the details of the ionic fragmentation patterns (such discussion can be found in the context of nanosecond and picosecond laser-induced fragmentation of C_6H_6 in Ref. [11]) and instead focus on the result that there is a surprising degree of similarity in the morphology of the ion-induced and light-induced fragmentation patterns.

B. Discussion

What lessons are to be drawn from our observations? Clearly, the first lesson is that the similarities in the mass spectra show that this correspondence is worthy of further pursuit, notwithstanding the ''obvious'' differences in the nature of the fields generated by nonrelativistic charged particle beams and pure electromagnetic radiation. The second lesson originates in the practical consideration that irradiation of matter by either type of field entails exposure to a *range* of field intensities; single-valued fields are encountered neither in nature nor in the laboratory. The spatial variation of field intensity gives rise to ''focal volume effects'' and makes it mandatory to ensure that equivalent intensity ranges are accessed in studies of field-matter interactions in order to make meaningful comparisons about the effects on the overall dynamics of the time duration of each type of field. We believe that we have succeeded in achieving this equivalence in our experiments. The somewhat surprising result to emerge is that, at least for C_6H_6, whether the intense field is of picosecond or attosecond duration is of little consequence as far as the overall ionic fragmentation pattern is concerned.

Thirdly, the other major difference between the two types of fields concerns their directional properties: the laser-induced field has a well-defined direction because the light is linearly polarized. But the direction of the ion-induced field changes in the course of the collision. Our data indicate that these properties seem unimportant to the overall dynamics. More work clearly needs to be done in order to develop further insights. However, it may be argued that for ion-induced fields (obtained using MeV ions) the change of direction is too fast to be of consequence. Even this postulate has an analog in the case of the laser-induced field ionization of molecules.

Recently, the effects of the polarization state of intense laser light on the spatial orientation of molecules have attracted much attention [12,13]. Strong dipole moments ($\boldsymbol{\mu}$) are formed when molecules are irradiated by light of intensity in excess of $\sim 10^{12}$ W cm^{-2}. With strong linearly polarized **E** fields, the induced dipole moments exert torques on the molecular axes, $\boldsymbol{\mu} \times \mathbf{E}$, that can be large enough to spatially reorientate molecules and their ions such that the most polarizable molecular axis points along the light field vector. In early experiments, anisotropic angular distribution of fragment ions that were obtained when the light polarization vector was rotated relative to the detector axis were taken to be signatures of spatial orientation [12]. Recently, it has been recognized that the molecular ionization rate depends on the angle that the internuclear axis makes with the light field vector, and that this also leads to anisotropic angular distributions [13]. Moreover, it is now established that laser pulse durations can become short enough for certain molecules not to align as there is simply not enough time for the $\boldsymbol{\mu} \times \mathbf{E}$ torque to act. A propensity rule has recently been proposed that allows predictions to be made of which molecules can be spatially aligned, and under what circumstances, upon irradiation by intense light, depending on parameters like the molecular polarizability, moment of inertia, peak intensity of the light, and its pulse duration [14]. Fields of attosecond duration, as in our ion-impact case, are certainly too fast for any spatial alignment to occur in C_6H_6.

Can our results be interpreted within the framework of molecular quantum mechanics? One attempt has been made to study intense laser-induced ionic fragmentation within the framework of molecular orbital energies [15], but application of fields that last only for, say, 30 as implies an energy uncertainty of ~ 22 eV. This makes quantal treatments of the ionization dynamics with conventional molecular states irrelevant.

ACKNOWLEDGMENTS

Gratitude is expressed to colleagues who have contributed to accelerator-based and intense-laser experiments over the years: F. A. Rajgara, V. R. Bhardwaj, G. Ravindra Kumar, U. T. Raheja, V. Krishnamurthi, C. Badrinathan, K. Vijayalakshmi, S. Banerjee, C. P. Safvan, M. Krishnamurthy, V. Kumarappan, E. Krishnakumar, K. Nagesha, and A. K. Sinha. The high-energy femtosecond laser was partially funded by the Department of Science and Technology. Some experiments were conducted at the Nuclear Science Center, New Delhi.

[1] D. Normand *et al.*, J. Phys. B **25**, L497 (1992); P. Dietrich *et al.*, Phys. Rev. A **47**, 2305 (1993); G.R. Kumar *et al.*, *ibid.* **53**, 3098 (1996); H. Stapelfeldt *et al.*, Phys. Rev. Lett. **79**, 2787 (1997); J.H. Posthumus *et al.*, J. Phys. B **31**, L553 (1998); W. Kim and P.M. Felker, J. Chem. Phys. **108**, 6763 (1998); J. Ortigoso *et al.*, *ibid.* **110**, 3870 (1999); S. Banerjee *et al.*, Phys. Rev. A **60**, R3369 (1999), and references therein.

[2] D. Mathur, Phys. Rep. **225**, 193 (1993); H.O. Folkerts *et al.*,

Phys. Rev. Lett. **77**, 3339 (1996); E. Wells *et al.*, Phys. Rev. A **60**, 3734 (1999); L. Adoui *et al.*, J. Phys. B **32**, 631 (1999); M. Tarisien *et al.*, *ibid.* **33**, L11 (2000).

[3] K. Boyer *et al.*, IEEE Trans. Plasma Sci. **16**, 541 (1988); T.S. Luk *et al.*, Phys. Rev. A **48**, 1359 (1993).

[4] V.R. Bhardwaj *et al.*, Phys. Rev. A **58**, 3849 (1998); **59**, 3105 (1999).

[5] D. Mathur *et al.*, Phys. Rev. A **50**, R7 (1994); J. Phys. B **27**, L603 (1994).

[6] J. D. Jackson, in *Classical Electrodynamics* (Wiley, New York, 1962), Chap. 15.

[7] S. Keller *et al.*, Phys. Rev. A **55**, 4215 (1997); R. Moshammer *et al.*, Phys. Rev. Lett. **79**, 3621 (1997).

[8] T. Tonuma *et al.*, J. Phys. B **17**, L317 (1984).

[9] A.S. Schlachter *et al.*, Phys. Scr., T **3**, 143 (1983).

[10] S. Banerjee *et al.*, J. Phys. B **32**, 4277 (1999).

[11] V.R. Bhardwaj *et al.*, Phys. Rev. A **59**, 1392 (1999); H.J. Neusser *et al.*, Int. J. Mass Spectrom. Ion Processes **60**, 147 (1984), and references therein.

[12] D. Normand *et al.*, J. Phys. B **25**, L497 (1992); P. Dietrich *et al.*, Phys. Rev. A **47**, 2305 (1993); G. Ravindra Kumar *et al.*, J. Phys. B **29**, L95 (1996); V.R. Bhardwaj *et al.*, Phys. Rev. A **56**, 2455 (1997), and references therein.

[13] J.H. Posthumus *et al.*, J. Phys. B **31**, L553 (1998); Ch. Ellert and P.B. Corkum, Phys. Rev. A **59**, R3170 (1999); S. Banerjee *et al.*, *ibid.* **60**, R3369 (1999).

[14] S. Banerjee, D. Mathur, and G. R. Kumar (unpublished).

[15] H. Rottke *et al.*, J. Phys. B **31**, 1083 (1998).