Quantum diagnosis of molecules: A method for measuring directly the Wigner function of a molecular vibrational state

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We propose a method for measuring directly the Wigner function of a molecular vibrational state. Our method does not involve the calculation of integral transforms, as in tomographic proposals, and is applicable to a large class of molecular states. [S1050-2947(98)08704-6]

I. INTRODUCTION

The possibility of manipulating and measuring the quantum state of a field or a particle has a wide range of implications, from testing fundamental laws of nature to bettering frequency standards. The state of a quantum system is given by its density operator, or equivalently by phase-space distributions (quasiprobabilities), which allow the calculation of quantum-mechanical averages of properly ordered products of operators as classical-like integrals of the corresponding c-number functions [1]. Therefore, the experimental determination of the density operator or of those phase-space distributions has been a major concern since the beginnings of quantum mechanics. Of special interest are those states displaying intrinsically quantum-mechanical behavior, which cannot be mimicked by classical distributions in phase space. These states are important not only for their definite quantum signature, but also because some of their properties make them specially suited to applications. This is the case, for instance, of squeezed states of light, which have been advocated for communications and precision measurements [2]. Progress in low-temperature techniques, ion traps, laser stabilization, cavity quantum electrodynamics, and atomic beams has led to many experiments in which particles or electromagnetic fields are prepared in intrinsically quantum states. Recent advances include the production and the detection of energy eigenstates and squeezed states of the center of mass of a trapped ion [3], of coherent superpositions of localized mesoscopic states of either the vibrational state of a trapped ion [4] or of an electromagnetic field in a cavity [5], and the measurement of the dynamics of molecular nuclear wave packets [6], including the determination of quasiprobabilities corresponding to the vibrational state of a diatomic molecule [7]. Furthermore, the density matrices and the Wigner functions [8] corresponding to various quantum states of motion of a trapped ion were experimentally determined by the NIST group [9]. From the theoretical point of view, an important breakthrough was obtained by K. Vogel and H. Risken [10], who showed how phase-space distributions for a mode of the electromagnetic field could be obtained from homodyne measurements made on the field. In this method, the Wigner function characterizing the state of the field is obtained from a tomographic Radon transform applied to the probability distributions for the quadratures of the field (marginal distributions of the Wigner function). The application of this procedure to determine the Wigner function of squeezed states of light has been very successful experimentally [11]. Other methods, also leading to the indirect determination of the Wigner function [12] or of the density matrix [13] through measurements of auxiliary quantities, have been proposed by several groups [14]. More recently, it was shown that the Wigner function of an electromagnetic field in a cavity or the vibrational state of a trapped ion could be directly measured, by a simple experimental procedure [15], which yields a physical meaning to that phase-space distribution, and eliminates the need of applying integral transforms to marginal distributions. Since this proposal for the direct measurement of the Wigner function was based on specific properties of the two systems considered, it is a nontrivial matter whether that idea could be extended to other systems. In this paper, we show that the Wigner function of the vibrational state of a molecule can also be directly measured. Our proposal is based on the same expression for the Wigner distribution as the one in [15]. The physics is, however, quite different, the specificities of the molecular system playing an important role in the present scheme. Other methods for reconstructing the state of molecular vibrations have been suggested in Refs. [16,17], including the case of anharmonic vibrations [17].

In the next section, we introduce the Wigner function for a molecular vibrational state, and express it in a convenient form, on which our further developments are based. In Sec. III, we describe the method for measuring directly the Wigner function of a molecular vibrational state. In Sec. IV, we discuss possible experimental procedures, and compare our proposal with other approaches. In Sec. V we simulate numerically a realization of the proposed method. Finally, in Sec. VI, we summarize our discussions.

II. CAHILL-GLAUBER FORM OF THE WIGNER FUNCTION

The Wigner function was introduced in 1932 by E. Wigner [8], who used it as a tool for calculating quantum corrections to classical statistical mechanics. For a particle with position q and momentum p in one dimension, it may be defined in terms of the corresponding density operator as

$$W(q,p) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} e^{ipx/\hbar} \left\langle q - \frac{x}{2} \middle| \rho \middle| q + \frac{x}{2} \right\rangle dx. \quad (1)$$

This function has the remarkable property that its integral with respect to q yields the momentum distribution of the particle, while the position probability density is obtained by integrating $W(q,p)$ with respect to p. Furthermore, as shown by Moyal [18], the quantum average of a Weyl-ordered (symmetric-ordered) function of the momentum and position operators can be expressed as a classical-like average of the corresponding classical function (in which the operators are replaced by c numbers), with the Wigner distribution acting as a weight measure in phase space. In spite of these properties, the Wigner function is not a bonafied probability distribution in phase space, as expected from the fact that Heisenberg's inequalities forbid the simultaneous measurement of the momentum and the position of a particle. In fact, for several states of the harmonic oscillator (including the energy eigenstates), $W(q,p)$ attains negative values. Nevertheless, we will show that the Wigner function corresponding to a molecular vibrational state can be directly measured.

For a harmonic oscillator, it is convenient to reexpress the Wigner function in terms of the raising and lowering operators A and $A^\dagger$, defined by $\hat{q} = \sqrt{\hbar/2m\omega}(A + A^\dagger)$, $\hat{p} = -i\sqrt{\hbar\omega m/2}(A - A^\dagger)$, where m and ω are the oscillator's mass and angular frequency, respectively. One gets then the Cahill-Glauber expression for the Wigner function corresponding to a density operator ρ, for a one-dimensional harmonic oscillator [1]:

$$W(\beta,\beta^*) = 2\,\mathrm{Tr}[\rho D(\beta,\beta^*) e^{i\pi A^\dagger A} D^{-1}(\beta,\beta^*)], \quad (2)$$

where β is a complex number characterizing an arbitrary point in phase space (and corresponding to the c-number version of operator A), and $D(\beta,\beta^*) = \exp(\beta A^\dagger - \beta^* A)$ is the displacement operator. This operator represents the action of a classical force acting on the harmonic oscillator: it yields the coherent state $|\beta\rangle$, an eigenstate of the lowering operator A with eigenvalue β, when applied to the harmonic oscillator ground state [19]. The function displayed in Eq. (2) is renormalized by the factor $2\pi\hbar$ with respect to the one defined by Eq. (1), so that $\int (d^2\beta/\pi) W(\beta,\beta^*) = 1$, where $d^2\beta \equiv d(\mathrm{Re}\beta)d(\mathrm{Im}\beta)$. Note that $W(\beta,\beta^*)$ is real. We show now how, with a sequence of electromagnetic pulses applied to a molecule, followed by the detection of the fluorescence, one can measure directly expression (2), as long as the vibrational potential can be approximated by a harmonic one.

III. DIRECT DETECTION OF THE WIGNER FUNCTION

We limit our discussion here to diatomic molecules for simplicity (our method can be extended to more complex configurations). Applicability of our method does impose some restrictions on the states involved, although there is still a large class of molecular levels that satisfy our requirements. We assume first that the potential interaction between the two nuclei may be approximated by a perfect one-dimensional harmonic oscillator. The oscillation direction is taken along the X axis. The equilibrium separation X_0^i and the frequency ω_i depend on the electronic state $|i\rangle$. The energy states of the molecule will be denoted by $|v,i\rangle$
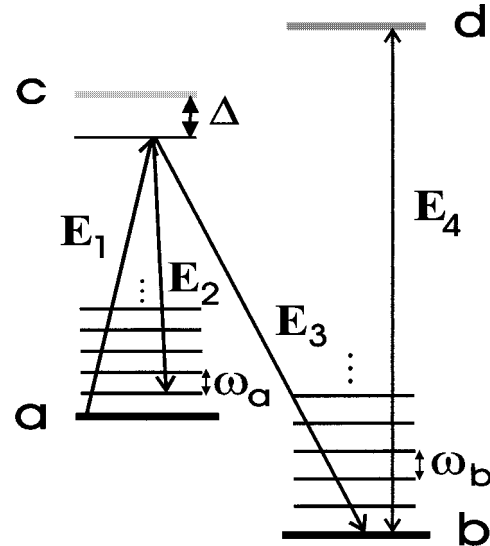

FIG. 1. Relevant level scheme. Raman transitions are driven between levels $|a,n\rangle$ and $|b,n'\rangle$ by switching on fields E_1 and E_3, and between levels $|a,n\rangle$ and $|a,n\pm 1\rangle$ by switching on instead fields E_1 and E_2. Field E_4 may be used eventually to detect the final state of the molecule.

$\equiv |v\rangle_i |i\rangle$, where $|v\rangle_i$ is the Fock state associated to v quanta of energy $\hbar\omega_i$. The displacement of the nuclei from the equilibrium position δX_i may be written in terms of the lowering and raising operators A_i and $A_i^\dagger$ as

$$\delta X_i = X - X_0^i = \left(\frac{\hbar}{2\mu\omega_i}\right)^{1/2}(A_i + A_i^\dagger), \quad (3)$$

where μ is the reduced mass of the two nuclei. When the electronic levels change, the atoms accommodate to another equilibrium distance and to a different ''spring constant.'' Therefore the vibronic Fock states associated to different electronic levels are related by a scale and a displacement transformation. For example, for two electronic levels $|a\rangle$ and $|b\rangle$,

$$|v\rangle_b = S(\lambda)D(\xi)|v\rangle_a, \quad (4)$$

where $S(\lambda) = e^{\lambda/2(A_a^2 - A_a^{\dagger 2})}$ is the squeezing operator [2] associated with the scaling factor $\lambda = \frac{1}{2}\ln(\omega_b/\omega_a)$ and $D(\xi)$ is the displacement operator $D(\xi) = e^{\xi(A^\dagger - A)}$. Here $\xi = (X_0^b - X_0^a)/\delta x_a$ is the displacement of X_0 in units of $\delta x_a = \sqrt{\hbar/2\mu\omega_a}$, the position uncertainty of the vibronic ground state associated with the electronic level $|a\rangle$.

The basic level scheme is illustrated in Fig. 1. States $|a,v\rangle$ and $|b,v'\rangle$ are coupled by a stimulated Raman transition via two classical fields. In the first part of the measurement process, fields E_1 and E_2 are applied, while in the second part E_2 is replaced by E_3. These fields are described by $E_k = E_k^0 e^{-i(\Omega_k t - \phi_k)} + \mathrm{c.c.}$, $k = 1,2,3$, and are detuned by Δ from the electric dipole transitions from $|a,v\rangle$ and $|b,v'\rangle$ to a third level $|c,v''\rangle$. We denote the energies of levels $|a,0\rangle$, $|b,0\rangle$, and $|c,0\rangle$ by $\mathcal{E}_a$, $\mathcal{E}_b$, and $\mathcal{E}_c$, respectively. A fourth level $|d\rangle$ may be used eventually to probe the populations of the two lower levels. The detuning Δ is defined by $\Delta = (\mathcal{E}_c - \mathcal{E}_a)/\hbar - \Omega_1$, while ω_a and ω_b are the vibrational

frequencies corresponding to the electronic levels a and b. When the frequency difference between the two beams E_1 and E_2 is tuned close to $\pm\omega_a$, there is a Rabi flopping between levels $|a,v\rangle$ and $|a,v\pm1\rangle$. On the other hand, application of the two fields E_1 and E_3, with $\Omega_3-\Omega_1$ tuned near $(\mathcal{E}_a-\mathcal{E}_b)/\hbar+\delta$, with $\delta=v\omega_a-v\omega_b$, leads to Rabi oscillations between levels $|a,v\rangle$ and $|b,v\rangle$ (Fig. 1).

We assume that $|\Delta|$ is much larger than δ, the Rabi frequencies associated to the dipole-allowed transitions, and the linewidths of levels a, b, and c, and at the same time much smaller than the transition frequencies from a and b to other levels, so that the contribution from c to the Rabi transition is by far the most important one. The effective Hamiltonian that describes the dynamics of these Raman transitions when fields E_k and E_ℓ are applied is given in the interaction picture by [20]

$$H'=\frac{1}{2}\sum_{i,j,v,v'}|i,v\rangle\langle j,v'|E_k^{0*}\cdot\vec{\vec{O}}_{vv'}^{ij}\cdot E_\ell^0\exp\{-i[(\mathcal{E}_i'-\mathcal{E}_j')/\hbar$$
$$+v\omega_i-v'\omega_j-\Omega_k+\Omega_\ell]t-i\varphi_{k\ell}\}+\text{H.c.}, \quad (5)$$

where $\varphi_{kl}=\phi_k-\phi_\ell$ and $\mathcal{E}_i'$ are the electronic energy levels a and b shifted by the virtual coupling to level c. When fields E_1 and E_2 are applied, only level a is shifted, while both a and b are shifted when E_1 and E_3 are applied. The coupling tensor $\vec{\vec{O}}_{vv'}^{ij}$ can be expressed in terms of the complex electronic polarizability tensor $\vec{\vec{\alpha}}^{ij}$ associated to the states i,j by

$$\vec{\vec{O}}_{vv'}^{ij}={}_i\langle v|\vec{\vec{\alpha}}^{ij}(R)|v'\rangle_j, \quad (6)$$

where $\vec{\vec{\alpha}}^{ij}$ is given by

$$\vec{\vec{\alpha}}^{ij}(R)=-\frac{2(q/m_e)^2}{\Delta\hbar\Omega_k\Omega_\ell}\int\psi_i(r,R)^*P\psi_c(r,R)d^{3v}r \quad (7)$$

$$\times\int\psi_c(r,R)^*P\psi_j(r,R)d^{3N}r. \quad (8)$$

In this expression, $\psi_i(r,R)$ is the wave function of the electronic level $|i\rangle$, which depends on both the N-electron coordinates (r) and the relative coordinates between the two atoms (R). The total electronic momentum operator is represented by P.

Let us suppose one wants to measure the Wigner function corresponding to the vibrational density operator ρ_{vib}, the initial state of the molecule being $\rho=\rho_{\text{vib}}\otimes|a\rangle\langle a|$. One first applies the two fields E_1 and E_2, with $\Omega_1-\Omega_2=\omega_a$. In this case, the electronic level does not change, and the relevant term in Eq. (5) is

$$H'=\frac{1}{2}|a\rangle\langle a|E_1^{0*}\cdot\vec{\vec{\alpha}}^{aa}(R_0)'\cdot E_2^0e^{-i\varphi_{12}}\left(\frac{\hbar}{2\mu\omega_a}\right)^{1/2}A_a^\dagger+\text{H.c.}, \quad (9)$$

where we have approximated $\vec{\vec{\alpha}}^{aa}(R)$ by

$$\vec{\vec{\alpha}}^{aa}(R)\approx\vec{\vec{\alpha}}^{aa}(R_0)+\vec{\vec{\alpha}}^{aa}(R_0)'(X-X_0^a), \quad (10)$$

the prime standing for the gradient in the X direction. If the two fields are applied during an interval of time equal

to τ, the density operator ρ_{vib} evolves to ρ_{vib}' $=D(\beta)\rho_{\text{vib}}D^{-1}(\beta)$ where $D(\beta)=e^{(\beta A_a^\dagger-\beta^*A_a)}$ is the operator that displaces a vibrational state in phase space by $\beta=-iE_1^{0*}\cdot\vec{\vec{\alpha}}^{aa}(R_0)'\cdot E_2^0e^{-i\varphi_{12}}(\hbar/2\mu\omega_a)^{1/2}\tau/2\hbar$ The ratio between the second and the first terms on the right-hand side of Eq. (10) is of the order of the ratio between the average vibrational amplitude of the nuclei and the spatial extent of the electronic wave functions [21].

After this first step we apply the fields E_1 and E_3, with $\Omega_3-\Omega_1=(\mathcal{E}_a'-\mathcal{E}_b')/\hbar+v(\omega_a-\omega_b)$, during an interval of time equal to τ'. If the frequencies ω_a and ω_b were equal, the transitions $|a,v\rangle\Leftrightarrow|b,v\rangle$ (same v) described by Eq. (5) would be at resonance for all v. This should be approximately true as long as $\delta\omega=|\omega_a-\omega_b|$ is not too large (we should have $1\ll\tau'\omega\ll\omega/\delta\omega$). The time evolution is described now by the effective Hamiltonian,

$$H'=\hbar\sum_v e^{-i\varphi_{13}}f_v|a,v\rangle\langle b,v|+\text{H.c.}, \quad (11)$$

where

$$f_v=\Omega_0\langle v|S(\lambda)D(\xi)|v\rangle, \quad (12)$$

and $\Omega_0=E_1^{0*}\cdot\vec{\vec{\alpha}}^{ab}(R_0)\cdot E_3^0/\hbar$. For $\lambda v,\xi^2v\ll1$, we may expand the coupling coefficient f_v and obtain

$$f_v=\Omega_0\left(1-\frac{\xi^2}{2}(1-\lambda)(1+2v)-\frac{\lambda^2}{4}(v^2+v+1)+\frac{\xi^4}{12}\left(3v^2\right.\right.$$
$$\left.\left.+4+\frac{3}{2}\right)+O(\lambda\xi^4v^2,\lambda^3v^3,\xi^6v^3,\lambda^2\xi^2v^3)\right). \quad (13)$$

We assume that the terms proportional to ξ^4 and λ^2 in Eq. (13) can be neglected (we will verify later that this is indeed the case for the molecules to be considered, as long as $v<10$). Defining $\chi=(1-\lambda)\xi^2$, and choosing $\chi\Omega_0\tau'=\pi$, so that $f_v\tau'/2=\Omega_0\tau'/2(1-\xi^2/2)+(\pi/2)v$, we have for the state of the system after the second step:

$$\rho''=[|a\rangle\cos(\Phi-\pi A_a^\dagger A_a/2)$$
$$+|b\rangle\sin(\Phi-\pi A_a^\dagger A_a/2)]\rho_{\text{vib}}'[\langle a|\cos(\Phi-\pi A_a^\dagger A_a/2)$$
$$+\langle b|\sin(\Phi-\pi A_a^\dagger A_a/2)],$$

where $\Phi=\Omega_0\tau'/2(1-\xi^2/2)$. From this expression we obtain the difference in the probabilities to find the molecule in the electronic states $|a\rangle$ and $|b\rangle$:

$$P_a-P_b=\cos(2\Phi)\text{Tr}[D(\beta,\beta^*)\rho_{\text{vib}}D(\beta,\beta^*)^{-1}e^{i\pi A_a^\dagger A_a}]$$
$$=\cos(2\Phi)W(-\beta,-\beta^*)/2. \quad (14)$$

The above equation is the central result of this work. It shows that determination of the difference in the probabilities of finding the molecule in states a and b, after the described sequence of pulses, leads to the direct measurement of the Wigner function of the vibrational state of the molecule. By changing the detuning Δ, as well as the amplitudes and relative phases of the fields E_1 and E_2, one may probe W

at different points β. In the following section, we discuss different possible experimental procedures, that may lead to the measurement of $P_a - P_b$.

IV. EXPERIMENTAL PROCEDURES

For each β, the probabilities P_a and P_b may be measured in the following way. The experiment is repeated several times, starting with the same initial state, and submitting the molecule to the same pulse sequence, after which one measures the fluorescence of the molecule. If $|a\rangle$ and $|b\rangle$ are both excited states, the frequency of the emitted radiation determines the state of the molecule at the end of each pulse sequence. This method works even if the light detection efficiency is poor, since experiments that lead to no counting should be discarded. This scheme should be changed, however, if $|b\rangle$ corresponds to the molecular ground state, since if no fluorescence is seen there are now two possibilities: either the molecule was in state $|b\rangle$ and no light was emitted, or it was in state $|a\rangle$, and the emitted light was not detected. In this case, one applies after each cycle the field E_4, which resonantly saturates the transition $|b\rangle \Leftrightarrow |d\rangle$. This scheme, used in recent ion trap experiments [4,9], leads to a fluorescence signal if the molecule is in state $|b\rangle$, while the absence of fluorescence implies that the ion is in $|a\rangle$ (since for a saturating transition the detection efficiency is close to 100%). We note that the same method can be applied when both a and b are excited states, as long as the duration of the pulse is smaller than the corresponding lifetimes.

An important feature of the scheme here proposed is that it does not require isolating a single molecule. It could be applied to a low-density ensemble of noninteracting molecules, as long as they are confined to a volume much smaller than the wavelengths of the fields involved, and they have the same initial state (this may require orientation of the molecular ensemble by an applied magnetic field). In this case, it is not necessary to repeat the pulse sequence in order to get the probabilities P_a and P_b. Indeed, if both a and b are excited levels, the fluorescence yields corresponding to their decays would be proportional to these probabilities! The proportionality constants depend on the oscillator strengths of these transitions. In practice, one may calibrate the detectors so that they yield the same result independently of whether the molecule is in state a or b. In this case, the difference in intensities, after a single cycle, will be proportional to the Wigner function at $-\alpha$. The proportionality constant can be evaluated either by determining the detection efficiency through an independent experiment, or by normalization of the obtained Wigner function. A similar scheme can be used if b is the molecular ground state. In this case, the intensity of the fluorescence resulting from the decay of level a would be directly proportional to the difference of probabilities $P_a - P_b$.

Our method would also work if the Raman processes are replaced by direct transitions. The advantage of the Raman scheme is that it allows for an easier calibration of the effective coupling constants involved. In some cases, however, depending on the levels involved, direct transitions might be preferable.

We consider now the classes of molecules to which our method could be applied. The basic requirements are: (i) the vibrational movement should be harmonic; (ii) the displacement of the potential should be small compared to the width of the vibronic ground state corresponding to the initial electronic level a; (iii) the change of the vibrational frequency should be small in the transition $a \leftrightarrow b$, compared with the inverse of the duration of the pulses E_1 and E_3; and (iv) the duration of theses pulses should span many vibrational cycles. The first condition implies that our method is specially suited to investigate lower vibrational states. On the other hand, the second and third conditions are satisfied for many molecular transitions.

It is interesting to compare our method with the pioneer work described in Ref. [7], where a phase-space distribution corresponding to the vibrational state of a sodium dimmer in an electronic excited state is tomographically reconstructed from measurements of the probability distributions of internuclear separations as a function of time. The measurements of the separations are obtained from the wavelength of the light emitted when the electron returns to the ground state. The method requires both a time and a frequency gate, implying from Fourier's theorem that it does not yield the Wigner function, but a blurred version of it. Because the measurement of internuclear separations relies on the position dependence of the emitted wavelength, the displacement of the vibration potentials corresponding to the ground and the excited states should not be small compared to the width of the vibrational ground state, in contradistinction to the assumption made here. Therefore, our proposal has a complementary role with respect to the procedure demonstrated in [7]. Besides, it leads directly to the Wigner function of the vibrational state.

V. NUMERICAL SIMULATION

Possible candidates to which our method could be applied are, for instance, many transitions in alkali metal atom dimers (Na_2, Rb_2, Cs_2, $RbCs$ . . .). We consider, as an example, the transitions involving the levels $4^3\Delta_g$ and $7^3\Delta_g$ of the Na_2 molecule. A thorough spectroscopic analysis of these levels has been recently done in Ref. [22] using optical-optical double resonance through the $A^1\Sigma_u^+ \sim b^3\Pi_u$ mixed levels. We use as working parameters the experimental results given in this reference [22]: $R_a = 3585$ Å, $R_b = 3567$ Å, $\omega_a/2\pi = 122.9 \text{ cm}^{-1}$, $\omega_b/2\pi = 121.9 \text{cm}^{-1}$. Using these parameters we have $|\xi| \approx 0.16$ and $\lambda \approx 0.0039$. The frequencies of the transitions $b^3\Pi_u \leftrightarrow 4^3\Delta_g$ and $b^3\Pi_u \leftrightarrow 7^3\Delta_g$ are in the region of the visible. Values of $|\beta|$ varying between 0 and 10 as well as values for $|\xi|^2\Omega_0\tau$ close to π may be easily reached for pulse durations smaller than the lifetimes of the levels involved, by changing the detuning Δ and the laser intensities.

In Ref. [22] the coefficients $Y_{2,0}$, $Y_{3,0}$, . . . in the Dunham expansion for the vibrational v dependence in the energy [21],

$$T_v = \sum_i Y_{i,0}(v + 1/2)^i,$$

were also obtained. Their values (for example, $-Y_{20}/Y_{10} < 0.004$) indicate that we may safely consider that the non-

harmonicity in the levels $4^3\Delta_g$ and $7^3\Delta_g$ is negligibly small as long as we consider an average number of photons not too large.

Using these values for the parameters, we have performed numerical simulations of experiments, following the procedure discussed in this paper. In these simulations, we do not approximate the function f_v given by Eq. (12), so that distortions of the detected distribution may occur. We have considered two different types of initial vibrational states, corresponding to either a coherent state or a Fock state. As we expect the difference between our results and the true Wigner functions are very small for the coherent state. For example, if $\bar{v}=5$ the relative error is always less than 0.5% in the region were $W(\beta,\beta^*)$ is greater than 0.01. When we have strongly nonclassical states like number states these errors may increase in certain regions of phase space. In Fig. 2 we show the function $W'(\beta,\beta^*)$ obtained by our simulation, together with the true Wigner function $W(\beta,\beta^*)$, when the initial vibrational state is a Fock state with $v=3$. We also show in this figure the difference $\Delta W(\beta,\beta^*)=W(\beta,\beta^*)-W'(\beta,\beta^*)$ between the true Wigner function and our simulation. We can see that although the errors may be relatively high in certain regions of phase space, they are larger just in those regions where the Wigner function changes sign. In particular, the largest absolute errors occur at $\beta=0$ when the quasiprobability function obtained by simulation is equal to -1.75 for $v=3$, instead of $W(0)=-2$. Also, the shape of the quasiprobability function obtained by the simulation has undoubtedly the characteristic features of the true Wigner function throughout the region of phase space considered in the simulation.

VI. CONCLUSIONS

In this paper, we have presented a method that allows the direct measurement of the Wigner function corresponding to a vibrational state of a molecule. Our method may be applied whenever the vibrational movement is well approximated by a harmonic potential (this requires in particular lower-lying vibrational states), and it requires furthermore that the initial molecular electronic level be connected via a direct or Raman transition to another electronic level such that the displacement of the vibrational potential is small compared to the width of the vibronic ground state corresponding to the initial electronic level. The change of the vibrational frequency should also be small compared with the reciprocal of the duration of the Raman pulses, which should in any case span many vibrational cycles. In spite of these restrictions, which give to this method a complementary aspect, with respect to the one adopted in the experiment reported in Ref. [7], there are yet many situations in which this method could be useful. It should be well suited, in particular, for analyzing vibrational states associated to highly excited Rydberg electronic levels. We have demonstrated that, even for a highly nonclassical vibrational state of the Na_2 molecule, the method still leads to a rather accurate determination of the corresponding Wigner function.

Either molecular beams or cells could be used for the implementation of the present proposal. We note, in particular, that recent developments in atomic traps have led to the
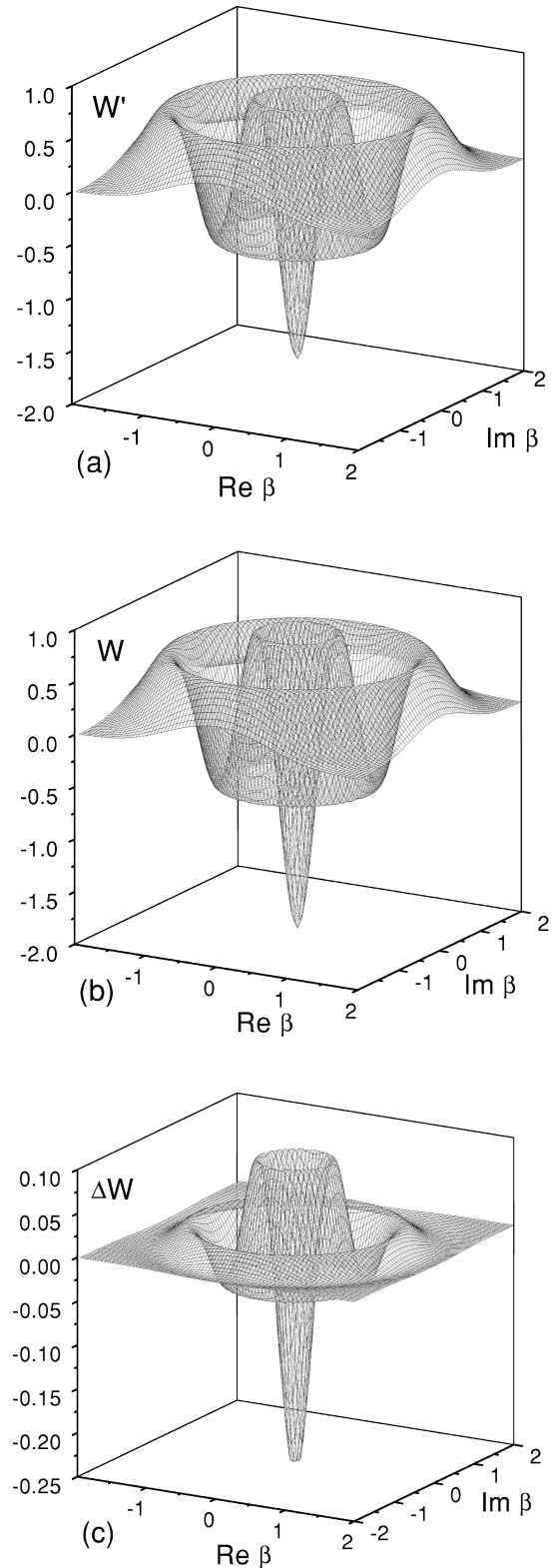

FIG. 2. Simulation of an experiment to measure a vibrational Fock state with $v=3$: (a) the function $W'(\beta,\beta^*)$ obtained in the simulation; (b) the true Wigner function $W(\beta,\beta^*)$; (c) the difference $W(\beta,\beta^*)-W'(\beta,\beta^*)$.

possibility of trapping molecules, specially paramagnetic ones [23]. Our method could be specially suited for the investigation of vibrational states of these trapped molecules.

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